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Laboratory and Field Evaluations of Extrasensitive Sulfur Dioxide and Nitrogen Dioxide Analyzers for Acid Deposition Monitoring

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16. ABSTRACT

Studies of environmental acid deposition require monitoring of very low levels of several atmospheric pollutants. Various passive and active samplers have been used to collect integrated atmospheric samples for such studies. Continuous analyzers offer an advantage because of their capability to provide more detailed information on the diurnal concentration patterns of the pollutants of interest. The U. S. EPA acquired two continuous NO_2 analyzer models (CSI 1600 and Scintrex LMA 3) and one SO_2 analyzer model (TECO 43S) with sufficient sensitivity to be potentially useful in studies of acid deposition. During the spring of 1988, RTI conducted laboratory and field evaluations of the extrasensitive analyzers. The analyzers' ranges were 0 to 50 ppb for the NO_2 analyzers and 0 to 10 ppb for the SO_2 analyzer. In the laboratory evaluation, performance parameters such as precision, limit of detection and interferences were quantitated. In the 31-day field evaluation, zero and span factor drafts and precision were quantitated. The results of the laboratory and field evaluations are given in this report. Although EPA has not established performance specifications for extrasensitive analyzers, the results of the laboratory and field evaluations suggest that the analyzers, generally, will perform in an acceptable fashion for the intended application. Nevertheless, several specific areas needing improvement were uncovered in the evaluations.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The U. S. Environmental Protection Agency's (EPA's; the Agency's) Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, has the responsibility for assessing environmental monitoring technology and systems; implementing agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air and Radiation, and the Office of Pesticides and Toxic Substances.

Studies of environmental acid deposition require monitoring of very low levels of several atmospheric pollutants. Various passive and active samplers have been used to collect integrated atmospheric samples. However, continuous analyzers would be greatly advantageous because of their capability to provide much more detailed information on the diurnal concentration patterns of the pollutants of interest. EPA has identified and purchased two continuous nitrogen dioxide analyzer models and one continuous sulfur dioxide analyzer model as potentially having sufficient sensitivity to be useful in acid deposition monitoring. These analyzer models were evaluated to definitively determine their specific applicability and acceptability for use in acid deposition monitoring applications. This report describes the analytical procedures that were used in laboratory and field evaluations of these analyzers. It also reports the test results that were obtained in the laboratory and field evaluations.

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NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under contract number 68-02-4550 to Research Triangle Institute. It has been subject to the agency's peer and administrative review, and it has been approved for publication as an EPA document.

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ABSTRACT

The objective of this project was to evaluate the performance characteristics of selected extra-sensitive NO_2 and SO_2 analyzers in both laboratory and field environments. The analyzers that were evaluated are two Columbia Scientific Industries (CSI) model 1600 NO_2 analyzers (on their 0-0.05 ppm range), two Scintrex model LMA 3 NO_2 analyzers (on their 0-50 ppb output range), and two Thermo Environmental (TECO) model 43S SO_2 analyzers (on their 0-10 ppb range). The laboratory test procedures for measuring performance characteristics were adapted from the equivalency test procedures given in Chapter 40, Part 53 of the Code of Federal Regulations. The field evaluation was conducted over an one-month period at a site in Research Triangle Park, North Carolina. The results of the laboratory and field evaluations are given in this report. Although EPA has not established performance specifications for extrasensitive analyzers, the results of the laboratory and field evaluations suggest that the analyzers, generally, will perform in an acceptable fashion for the intended application. Nevertheless, several specific areas needing improvement were uncovered in the evaluations.

This report is submitted in fulfillment of EPA contract no. 68-02-4550, work assignment 18. This report covers a period from January 1 to August 10, 1988.

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SECTION 1
INTRODUCTION

The objective of this project, EPA contract no. 68-02-4550, work assignment 18, was to evaluate the performance characteristics of selected extrasensitive nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) analyzers in both laboratory and field environments. The laboratory NO_2 evaluation was performed from February 23 to March 24, 1988. The laboratory SO_2 evaluation were performed from April 5 to April 19, 1988. The field evaluation was performed from April 26 to May 27, 1988.

The analyzers that were evaluated are two Columbia Scientific Industries (CSI) model 1600 NO_2 analyzers, two Scintrex model LMA 3 NO_2 analyzers, and two Thermo Environmental (TECO) model 43S SO_2 analyzers. The CSI model 1600 NO_2 analyzers detect NO_2 by catalytic conversion of NO_2 to nitric oxide (NO) followed by the chemiluminescent reaction of NO with ozone (O_3). This method, referred to as gas-phase chemiluminescence, is currently the specified EPA reference measurement principle for the measurement of NO_2 in the atmosphere (1). The Scintrex model LMA 3 NO_2 analyzers detect NO_2 by the chemiluminescent reaction with luminol in aqueous solution. During all tests, both LMA 3 analyzers sampled through ozone traps which were supplied by Scintrex. The TECO model 43S SO_2 analyzers detect SO_2 by ultraviolet fluorescence (UVF) using a pulsed light source. Ultraviolet fluorescence is being considered as a measurement principle to supersede the current EPA Reference Method for SO_2 (pararosaniline method). The ranges that the instruments were tested on are as follows:

CSI model 1600 NO_2	0-0.05 part per million (ppm) (i.e, 0-50 ppb),
Scintrex model LMA 3 NO_2	0-50 ppb at recorder output, (0-20 ppb on front panel meter), and
TECO model 43S SO_2	0-10 parts per billion (ppb).

Each instrument also has higher ranges which were not used in this evaluation.

Before evaluating the analyzers' performance characteristics, it was necessary to consider what characteristics are relevant to performance and how those characteristics can be experimentally measured. Performance specifications and acceptance tests for ambient air quality monitoring equipment have been established in the Code of Federal Regulations (2). These specifications are referred to as "equivalency specifications". In general, the procedures used in the laboratory and field evaluations are modified versions of the tests given in the equivalency specifications.

A fundamental difference exists between the purpose of the equivalency specifications and the purpose of the present study. The equivalency specifications were designed to certify that a given instrument was acceptable for determining the compliance of a locality with the National Ambient Air Quality Standards (NAAQS) for the given pollutant (1). Performance specifications were established for these methods and test procedures were given to determine whether an instrument demonstrated acceptable performance (2). The purpose of the current study was to evaluate instruments with substantially better sensitivity than those used for compliance monitoring. No similar performance specifications exist for these extrasensitive instruments. Thus, this evaluation estimated the performance parameters of the instruments quantitatively rather than determining whether these instruments met predefined specifications. It was necessary for the tests employed to produce a numerical estimate of the performance parameters. For this reason, many of the tests described in reference 2 were modified for this study. These tests are described in a following section.

In addition to the laboratory tests for evaluating performance parameters, a field evaluation of the instruments was performed. The field evaluation was conducted over a 31-day period at RTI's Material Exposure Site in Research Triangle Park, North Carolina. The CSI 1600, LMA 3 and TECO 43S extrasensitive analyzers and other analyzers at the site were operated under typical ambient air quality monitoring conditions. This portion of the study provided a real-world evaluation of the extrasensitive analyzers' performance. The primary goals of the field evaluation were to measure the analyzers' zero and span drifts and their precision.

SECTION 2
SUMMARY AND CONCLUSIONS

A summary of the results of the laboratory evaluation (excluding the interference tests) is given in Table 1. The results of the interference tests are given in Section 5.

EPA has not established performance specifications for extrasensitive analyzers to be used in acid deposition monitoring. As a result, conclusions concerning the specific applicability and acceptability of these analyzers cannot be drawn. Nevertheless, general conclusions based on the current test results have been drawn and are presented in the following paragraphs.

MAINTENANCE AND FAILURES

During the laboratory evaluation, the CSI 1600 and TECO 43S analyzers required only scheduled maintenance and experienced no operational failures. One LMA 3 analyzer experienced problems with fluid backup in the air intake trap. The problem was traced to worn pump tubing and a misaligned tensioning bracket on the pump. Realigning the bracket and replacing the tubing at two-week intervals solved that problem. Erratic responses were noted after several days operation of the LMA 3 analyzers. This problem was eliminated by backflushing the LMA 3 analyzers on a daily basis.

During the field evaluation, the TECO 43S and CSI 1600 analyzers required only scheduled maintenance. One CSI 1600 analyzer experienced a temporary failure in its NO_x channel due to an air conditioner failure at the field site. All three analyzers experienced noticeable but temporary changes in calibration during the air conditioner failure. One LMA 3 analyzer had a solution backup into its ozone trap. It is possible that an earlier replacement in pump tubing could have prevented this problem.

INTRA-MODEL AGREEMENT

In general, the values of the performance parameters for the two analyzers within a given model showed good agreement during the laboratory evaluation. The only noticeable lack of agreement was for the precision estimates. One analyzer of each model had somewhat greater precision estimates than had the other analyzer in that model. For the nitrogen dioxide analyzers, the intra-model agreement was better than the inter-model agreement.

From the field evaluation data, the intra-model agreement is estimated by the concentration difference between the hourly average concentrations indicated by the two analyzers within a given model. The 30-day, overall mean concentration difference for the LMA 3 analyzers is 0.733 ppb. On a daily basis, the mean concentration difference varies from -1.577 to 1.793 ppb. The pattern of the day-to-day variation in the mean concentration differences parallels the pattern of the day-to-day variation in LMA B's span factor (see below). The two phenomena appear to be related in some manner.

Table 1. Summary of Results for the Laboratory Evaluation of Extrasensitive SO_2 and NO_2 Analyzers (excluding interference tests)

Performance Parameter	Units	Nitrogen Dioxide Analyzers				Sulfur Dioxide Analyzers	
		LMA A	LMA B	CSI A	CSI B	TECO A	TECO B
Mean Noise (am)	ppb	0.003	0.004	0.280	0.335	0.032	0.016
Mean Noise (pm)	ppb	0.002	0.003	0.303	0.358	0.033	0.015
Mean Precision (0% FS)	ppb	0.003	0.003	0.221	0.363	0.029	0.016
Mean Precision (20% FS)	ppb	0.040	0.050	0.300	0.408	0.038	0.017
Mean Precision (50% FS)	ppb	0.065	0.078	0.300	0.364	0.046	0.027
Mean Precision (80% FS)	ppb	0.105	0.165	0.297	0.426	0.052	0.035
Limit of Detection[a]	ppb	0.009	0.009	0.663	1.089	0.088	0.049
Limit of Quantitation[a]	ppb	0.030	0.030	2.210	3.630	0.292	0.163
Lower Detection Limit	ppb	0.005	0.006	0.560	0.670	0.065	0.031
Mean Daily Zero Drift (am)	ppb	-0.00	0.00	0.01	0.04	0.010[b]	0.003[b]
Mean Daily Zero Drift (pm)	ppb	-0.00	-0.00	-0.00	0.02	0.011[b]	0.003[b]
Mean Daily Span Drift (20% FS)	%	-1.3	-3.3	0.3	0.1	0.1[b]	0.7[b]
Mean Daily Span Drift (50% FS)	%	0.4	-1.2	0.6	0.6	0.4[b]	0.7[b]
Mean Daily Span Drift (80% FS)	%	0.7	-0.5	0.5	0.3	0.5[b]	0.8[b]
Mean Daily Span Factor Drift	%	-1.0	-0.0	-0.6	-0.4	-0.4	-0.9
Mean Rise Time	min	1.8	1.9	4.9	4.3	3.5	3.4
Mean Fall Time	min	0.2	0.3	4.2	3.8	3.4	3.5

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[a] These values are calculated from the mean precision at 0% FS. Slightly higher values for the LMA 3 and TECO analyzers are obtained when the concentration-dependent precision estimates are used.

[b] Higher values for the zero and span drifts are obtained when Days 3 and 7 are excluded from the calculations. These revised zero and span drifts are equivalent to approximately -1.1% FS per day.

The overall mean concentration difference for the CSI 1600 analyzers is -0.259 ppb. On a daily basis, the mean concentration difference varies from -1.134 to 0.212 ppb. The daily mean values are generally consistent from the beginning of the field evaluation (Julian day 117) through Julian day 132 and show greater variability afterwards.

The overall mean concentration difference for the TECO 43S analyzers is 0.036 ppb. On a daily basis, the mean concentration difference varies from -0.008 to 0.112 ppb. Relatively little day-to-day variation is seen in these daily mean values.

NOISE

The LMA 3 NO_2 analyzers had considerably less noise than the CSI 1600 NO_2 analyzers. The noise level for the TECO 43S SO_2 analyzers was between that of the two NO_2 analyzer models. During the field evaluation, ambient air measurements using the LMA 3 analyzers exhibited more short-term variability than the corresponding measurements for the CSI 1600 analyzers. However, the LMA 3 analyzers' responses were less noisy during field calibration than those of the CSI 1600 analyzers. It appears that the LMA 3 analyzers were responding to short-term fluctuations in the ambient air NO_2 concentration which were being integrated over longer time periods by the CSI 1600 analyzers.

PRECISION

In the laboratory evaluation, the LMA 3 NO_2 analyzers had lower precision values (i.e. better precision), expressed as standard deviation than the CSI 1600 NO_2 analyzers. The precision values for the LMA 3 NO_2 analyzers increased with increasing concentration. The precision values for the CSI 1600 NO_2 analyzers did not exhibit a concentration dependence. The precision values for the TECO 43S SO_2 analyzers were lower than those of the NO_2 analyzers and showed a concentration dependence.

From the field evaluation data, estimates of the intra-model precision and the effective operating precision are calculated. The first estimate is obtained by dividing the standard deviation of the concentration differences between the two analyzers within a given model by the square root of 2. The precision estimate is somewhat in error for the LMA 3 and TECO 43S analyzers because of its assumption that the precision is independent of concentration. The laboratory evaluation demonstrated that the precision of these analyzers is concentration dependent. The second estimate is obtained from the principal component analysis program that was developed by Holland and McElroy (25). The second estimate includes both the intra-model precision and the uncertainty associated with assumed random interference effects.

The overall standard deviation of the concentration differences between the two LMA 3 analyzers is 0.930 ppb, which results in an intra-model precision estimate of 0.658 ppb. On a daily basis, the standard deviation varies from 0.091 to 1.901 ppb. This precision estimate may be influenced by the day-to-day variation in LMA B's span factor (see below).

The overall standard deviation of the concentration differences between the two CSI 1600 analyzers is 0.554 ppb, which results in an intra-model precision estimate of 0.392 ppb. On a daily basis, the standard deviation varies from 0.149 to 1.039 ppb.

The overall standard deviation of the concentration differences between the two TECO 43S analyzers is 0.042 ppb which results in an intra-model precision estimate of 0.030 ppb. On a daily basis, the standard deviation varies from 0.012 to 0.061 ppb.

It should be noted that these intra-model precision estimates cannot be compared validly to those obtained during the laboratory evaluation. The field estimate is for hourly average measurements of varying concentrations and the laboratory estimate is for instantaneous measurements of a constant concentration. Nevertheless, the estimate for the LMA 3 analyzers obtained from the field evaluation data is approximately an order of magnitude greater than those obtained from the laboratory evaluation data. The difference between the laboratory and the field precision estimates that is seen for the LMA 3 analyzers is not seen for the CSI 1600 and TECO 43S analyzers. The laboratory and field precision estimates are in good agreement for the latter analyzers.

The effective operating precisions of the extrasensitive analyzers during the field evaluation were calculated using the principal component analysis program that Holland and McElroy developed. The hourly mean concentrations were used inthe calculations. THis statistical method has a number of assumptions which must be satisfied if its results are to be statistically valid. Among these assumptions are:

- At least three analyzers' data must be compared;
- The range of measured concentrations is large relative to the precision;
- The precision must be concentration-independent;
- The interference effect must be random and independent of the pollutant concentration; and
- The analyzers to be compared must be sufficiently different in their sensitivity to interfereing substances.

These assumptions are violated to some degree by the extrasensitive analyzer data from the field evaluation. Accordingly, precision estimates from principal component analysis of these data are somewhat questionable.

The effective operating precisions for the two LMA 3 analyzers are 0.504 and 0.628 ppb, which compare well with the corresponding intra-model precision of 0.658 ppb. These precision estimates may be partially compromised by the span factor drift that was observed in LMA B. The frequent calibration of these analyzers tended to reduce the effect of this drift on the NO_2 concentration measurements and the precision estimates obtained from these analyzers.

The effective operating precisions for the two CSI 1600 analyzers are 0.284 and 0.185 ppb, which are appreciably lower than the corresponding intra-model precision of 0.392 ppb.

These values are considerably lower than the value of 2.7 ppb obtained by Holland and McElroy for the same analyzer model (25). Their data set was collected on the analyzer's 0 to 500 ppb range, while this data set was collected on its 0 to 50 ppb range. The range that is used may have an effect on the analyzer's precision.

The principal component analysis of the SO_2 data included measurements from the RTI trailer's TECO model 43A SO_2 analyzer. This analyzer was calibrated using a different calibration apparatus from that used for the extrasensitive analyzers. It was operated on its 0 to 200 ppb FS range. This inclusion was necessary to satisfy the requirement of principal component analysis that at least three analyzers' data must be compared.

The effective operating precisions for the TECO 43S analyzers are 0.0003 and 0.0003 ppb, which are approximately two orders of magnitude less than the corresponding intra-model precision of 0.030 ppb. It is hypothesized that the small precision estimate from principal component analysis is a result of violating the assumption that the analyzers to be compared must be different. The effective operating precision for RTI's TECO 43A analyzer is 0.111 ppb.

DETECTION LIMITS

The detection limits for the LMA 3 NO_2 analyzers were lower than those of the CSI 1600 NO_2 analyzers. There was only a very small difference between of the detection limit estimates for the LMA 3 NO_2 and TECO 43S analyzers with and without compensation for their increase in precision with concentration. The detection limits for the TECO 43S SO_2 analyzers were between those for the two NO_2 analyzer models.

ZERO AND SPAN DRIFTS

Analysis of the zero and span factors that were obtained during the laboratory evaluation for the CSI 1600 NO_2 analyzers did not show any obvious dependence on room temperature or line voltage. In addition, no time-dependent change (secular trend) of either zero values or span factors was seen for the CSI 1600 analyzer.

The LMA 3 NO_2 analyzer showed a slight dependence of zero values on temperature (approximately -0.003 to -0.006 ppb/degree C). This is in agreement with the value of -0.009 ppb /degree C obtained by Bubacz and Pleil (3). The LMA 3 analyzers did not show the temperature dependent span drift seen in earlier models by Bubacz and Pliel (3). No secular trend or voltage dependence in zero or span drift was seen for the LMA 3 analyzer.

The TECO 43S analyzers showed a secular trend in their zero values of approximately -0.1 ppb/day during the laboratory evaluation. This made the span values appear to also drift because the span drift calculations do not provide for a zero-drift correction. In addition, the TECO 43S analyzers' zero values showed a slight dependence on temperature (approximately 0.024 ppb/degree C). No change in span factors with time, temperature, or line voltage was seen for the TECO 43S analyzer.

During the field evaluation, no secular trends were observed in the zero values for the CSI 1600 and LMA 3 analyzers. The TECO 43S analyzers showed a secular trend in their zero values of approximately -0.01 ppb/day. This trend is approximately an order of magnitude less than that observed during the laboratory evaluation in these same analyzers. No secular trends were observed in the span factors for the CSI 1600 analyzers and one of the two LMA 3 analyzers. The other LMA 3 analyzer exhibited a span factor drift of approximately 2.2%/day. It is hypothesized that this drift was caused by excessive wear in the analyzer's pump tubing because large span factor shifts were observed when the pump tubing was replaced in this analyzer. The two TECO 43S analyzers exhibited span factor drifts of approximately -0.13 and -0.28%/day.

RISE AND FALL TIMES

All the extrasensitive analyzers' rise and fall times were within 5 minutes. The LMA 3 NO_2 analyzers' values were noticeably faster than those of the other extrasensitive analyzers. Additionally, the fall times for the LMA 3 NO_2 analyzers were much faster than the corresponding rise times.

The LMA 3 NO_2 and TECO 43S SO_2 analyzers took long periods of time (i.e., several hours) to rise from approximately 95 to 100 percent of their final, stable readings during each test day's initial change from an overnight zero air exposure to an 80-percent full scale concentration. This phenomenon was not observed for the CSI 1600 NO_2 analyzers. In the case of the LMA 3 NO_2 analyzers, it is hypothesized that their ozone traps required conditioning. In the case of the TECO 43S SO_2 analyzers, it is hypothesized that this phenomenon is associated with the daily initial conditioning of the calibration apparatus and the sample lines after the overnight zero air exposure. This phenomenon was not observed after subsequent step concentration changes during each test day.

INTERFERENCES

Each of the extrasensitive analyzer models responded to one or more interferents. The LMA 3 NO_2 analyzers responded to oxygen, carbon dioxide, water, PAN, and nitrous acid. The relative response to PAN was lower than the quantatative response reported by Wendell et. al. (4). The nitrous acid interference has not been reported previously in the literature. Interference from O_3 on luminol-based chemiluminescent analyzers, which was reported in the literature (4, 5), was not seen in this study with the LMA 3 analyzers. It appears that the O_3 traps which were supplied by Scintrex are effective in eliminating the O_3 interference in the LMA 3 NO_2 analyzers. The CSI 1600 NO_2 analyzers showed responses to water, ammonia, PAN, nitric acid, and nitrous acid. The ammonia response was not found in a previous post-designation equivalency testing of the CSI 1600 NO_2 analyzer. It is hypothesized that insufficient test manifold stabilization time was allowed in the earlier testing. The TECO 43S SO_2 analyzer responded to nitric oxide and xylene. The nitric oxide response was greater than what has been reported by TECO for the model 43A SO_2 instrument.

AMBIENT AIR QUALITY MEASUREMENTS

The field evaluation was conducted from April 26 through May 27, 1988. During this period, the CSI 1600 and LMA 3 analyzers produced 483 sets of matched hourly mean NO_2 concentrations. The TECO 43S and TECO 43A analyzers produced 463 sets of matched hourly mean SO_2 concentrations during the same period. Overall mean concentrations for the field evaluation are as follows:

Parameter	Analyzer	Overall Mean Concentration
NO_2	CSI A	13.022 ppb
	CSI B	13.314 ppb
	LMA A	11.309 ppb
	LMA B	10.512 ppb
SO_2	TECO A	1.691 ppb
	TECO B	1.653 ppb
	RTI-SO_2	1.398 ppb

The SO_2 data are in good agreement with SO_2 data collected with a filter pack at a nearby EPA National Dry Deposition Network site in Research Triangle Park. The EPA site measured an overall mean SO_2 concentration of 1.61 ppb for the period from April 26 through May 24, 1988.

CALIBRATION APPARATUS

It was necessary to design and fabricate a calibration apparatus for the laboratory and field evaluations that is capable of generating ppb-level SO_2 and NO_2 concentrations. In general, the effort was successful. The laboratory evaluation demonstrated that the apparatus could generate NO_2 at low concentrations via gas phase titration. It also demonstrated that the turbulent mixing loop permits the rapid concentration changes needed for response time measurements. The daily span factors from the field evaluation demonstrated that the calibration apparatus has good repeatibility on a day-to-day basis. However, it was not possible to evaluate the accuracy of the concentrations that the calibration apparatus generated.

The only negative feature of the calibration apparatus that was discovered is the long stabilization time (approximately 2 hours) for the TECO 43S SO_2 analyzers. After an overnight zero air exposure and the initial change to a 80-percent full scale concentration, the TECO 43S SO_2 analyzer took a long time to go from 95-percent to 100-percent of the final, stable reading. This phenomenon was not observed for subsequent step concentration changes during each test day. It is hypothesized that the long stabilization time is due to the need to condition the PFA Teflon™ walls of the calibration apparatus after the overnight zero air exposure.

A similar phenomenon was observed for the LMA 3 NO_2 analyzers, but it is not attributed to the calibration apparatus because it was not seen for the CSI 1600 NO_2 analyzers. It is hypothesized that the LMA 3 NO_2 analyzers' ozone traps required conditioning.

SECTION 3
RECOMMENDATIONS

Performance specifications should be established for extrasensitive analyzers to be used in acid deposition monitoring. Users of monitoring data obtained with these extrasensitive analyzers should be made aware of the performance characteristics of the analyzers (especially with respect to interference effects).

To prevent changes in O_2 concentration from affecting analyzer response, calibration mixtures for all three types of instruments should be made using dilution with air rather than nitrogen or another dilutant. In addition, the the LMA 3 NO_2 analyzer is sufficiently sensitive to O_2 concentration that the percentage of O_2 in synthetic zero air must be closely specified. Similarly, the CO_2 and water concentrations of calibration mixtures for the LMA 3 NO_2 analyzer should be similar to those in ambient air to prevent changes in analyzer response due to differing concentrations of CO_2 and water. The water concentration of calibration mixtures for the CSI 1600 NO_2 analyzer should be similar to that in ambient air to prevent interference effects. Sites using the TECO 43S SO_2 analyzer should monitor NO concentrations to be able to detect and possibly correct for NO interference.

Sites using the LMA 3 NO_2 analyzer should backflush the analyzer daily and change the pump tubing every two weeks to prevent operational failures. All three types of instruments should be operated in buildings with heating and air conditioning, as evidenced by the temporary change in zero and span values which occurred when the air conditioner at the Materials Exposure Site malfunctioned.

Further investigations of some of the instrumental characteristics revealed in this laboratory evaluation should be pursued. In particular, more extensive interference tests may be needed for those compounds which demonstrated an interference in this study. Additional work is needed to identify the cause of the span drift observed in one LMA 3 NO_2 analyzer during the field evaluation.

SECTION 4
TEST PROCEDURES

GENERATION OF ATMOSPHERES CONTAINING ANALYTE

Zero air

Zero air for the laboratory evaluation was prepared by compressing, filtering, and scrubbing ambient air. The air was compressed with an oilless compressor, and then was filtered, and dried with permeation and silica gel driers. The dried air was then passed over an heated oxidizing catalyst column (0.5 percent palladium on alumina spheres at approximately 175 degrees Celsius) to convert hydrocarbons and carbon monoxide (CO) to carbon dioxide (CO_2). The air was then passed over a Purafil(TM) column (potassium permanganate-coated alumina spheres) to convert NO to NO_2, which is sorbed by Purafil(TM). The Purafil(TM) treated air was dried with silica gel to remove any water produced, was passed through activated charcoal, and was filtered through a spun fiberglass filter. Zero air for the field evaluation was prepared in a similar manner except that no heated catalyst bed was used.

Test manifold

The test manifold for laboratory evaluation (Figures 1 and 2) was made from 1.27-cm OD (0.95-cm. ID) PFA Teflon(TM) tubing. Calibration mixtures flowed through the manifold at a volumetric flow rate of 10 standard liters per minute (SLPM), which corresponds to a linear velocity of 234 centimeters per second and a Reynold's number of approximately 1470. One end of the test manifold was open and was vented to an outside vent at atmospheric pressure. The test atmospheres were prepared as described below and were delivered to the test manifold at atmospheric pressure. The analyzers were connected to the test manifold with 0.64-cm. OD (0.40-cm. ID) PFA Teflon(TM) tubing. All tubing lengths were kept as short as possible to reduce sorption losses.

A 36-cm. length of 0.32-cm. OD (0.17-cm. ID) PFA Teflon(TM) tubing was used to connect the test atmosphere generation apparatus with the test manifold. This narrow diameter connecting tubing provides turbulent mixing (Reynold's number of approximately 8220 at 10 L/min total flow) of the pollutant gases and zero air. A calculation based on eddy diffusion coefficients indicated that greater than 99% mixing should take place (6). The use of a turbulent mixing loop, as opposed to a mixing bulb, avoids the long time delays associated with a large mixing volume. This feature of the manifold is important for measurement of analyzer response times. The translucent portion of the manifold was covered with aluminum foil to avoid NO_2 photolysis.

This test manifold was also used to prepare calibration mixtures for the field evaluation (Figure 3). It was not used for the ambient air measurements during the field evaluation. The extrasensitive analyzers were connected to the trailer's glass sampling manifold for ambient air measurements. This ensured that all analyzers operated by RTI were sampling through the same manifold for comparison purposes.

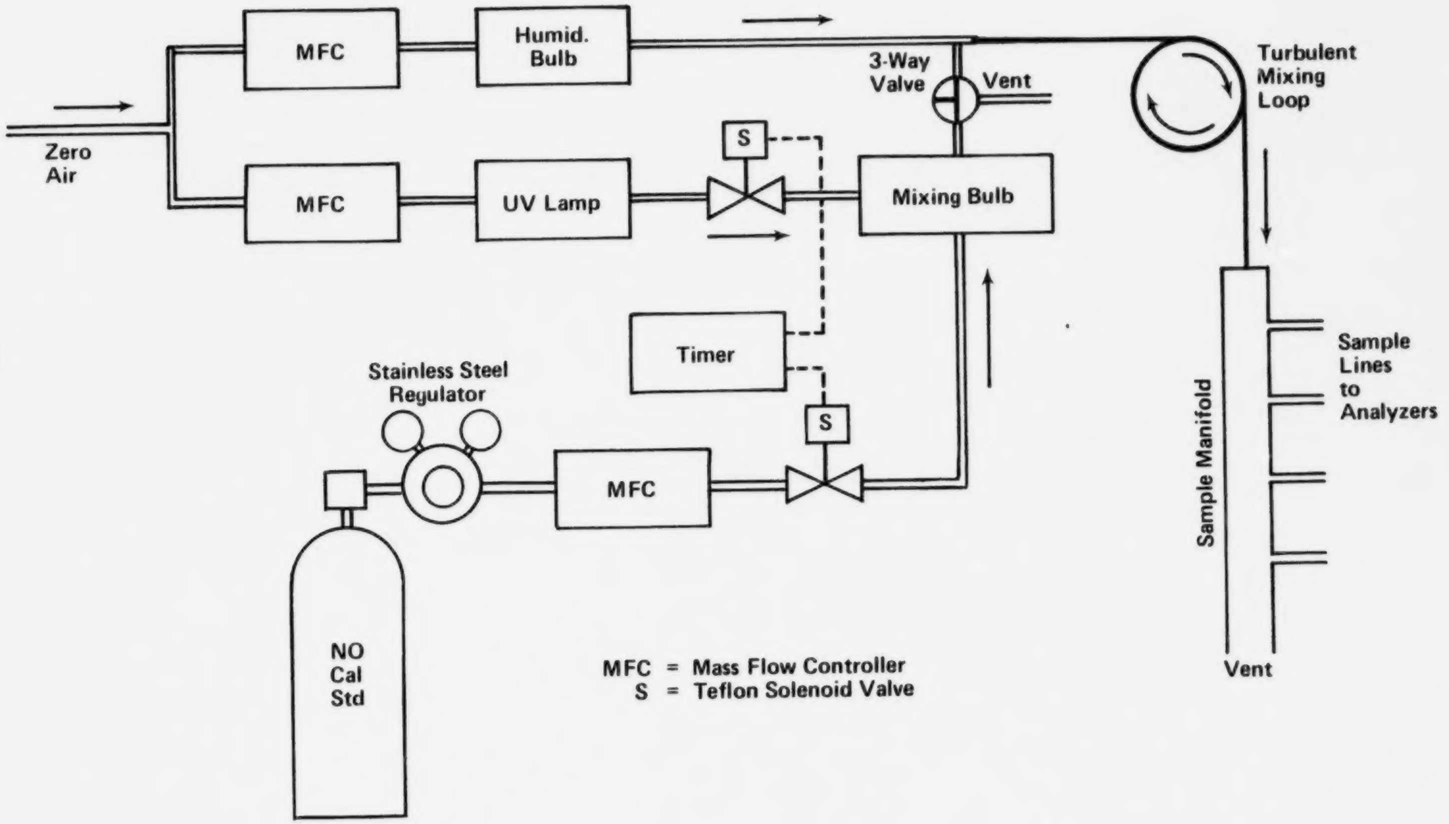

Figure 1. NO_2 generation apparatus.

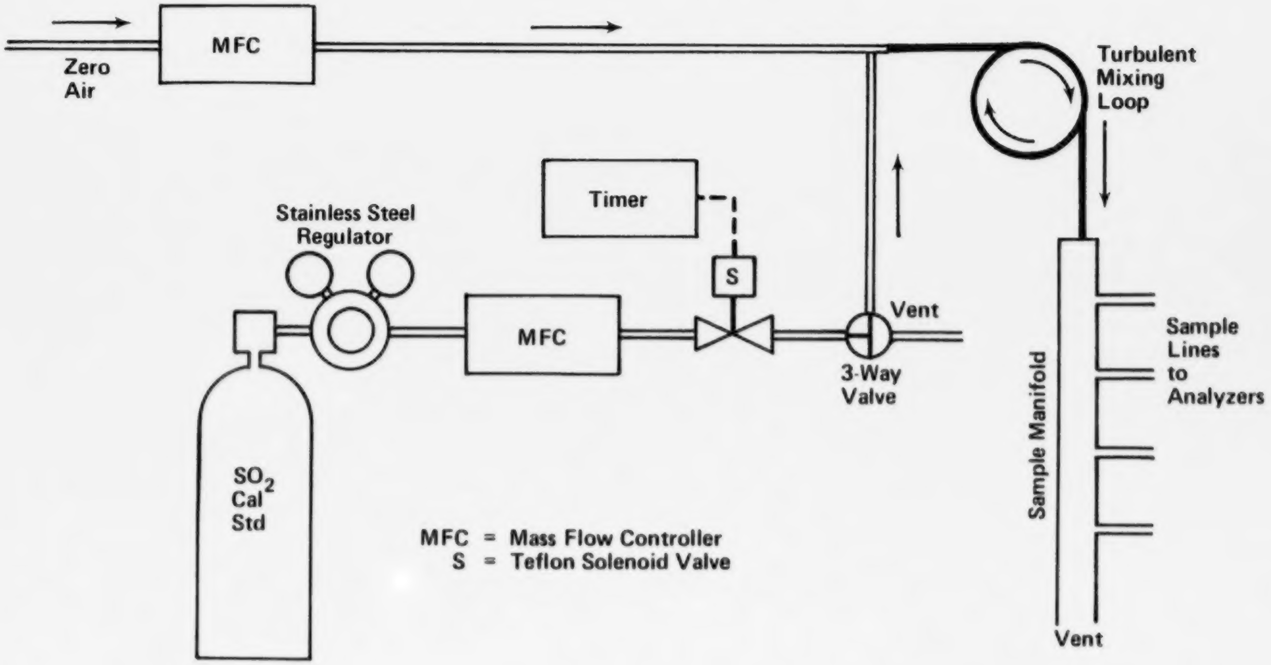
Zero Air
MFC
Turbulent Mixing Loop
Stainless Steel Regulator
Timer
S
MFC
Vent
3-Way Valve
Sample Manifold
Sample Lines to Analyzers
Vent
SO_2 Cal Std
MFC = Mass Flow Controller
S = Teflon Solenoid Valve

Figure 2. SO_2 generation apparatus.

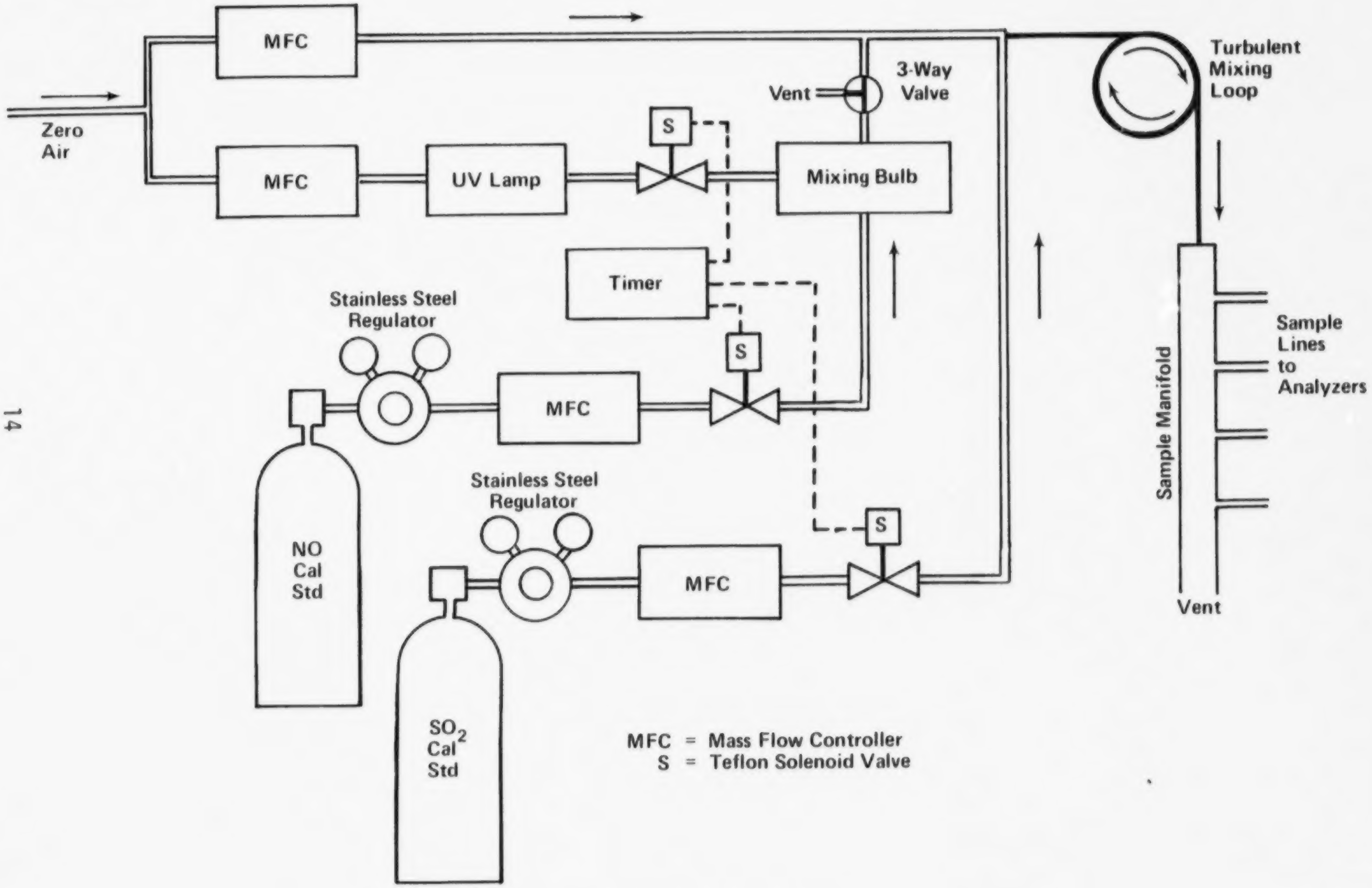
Zero Air
MFC
MFC
UV Lamp
S
Mixing Bulb
Vent
3-Way Valve
Turbulent Mixing Loop
Timer
S
Stainless Steel Regulator
MFC
NO Cal Std
Stainless Steel Regulator
S
MFC
SO_2 Cal Std
Sample Manifold
Sample Lines to Analyzers
Vent
MFC = Mass Flow Controller
S = Teflon Solenoid Valve

Figure 3. Field calibration apparatus.

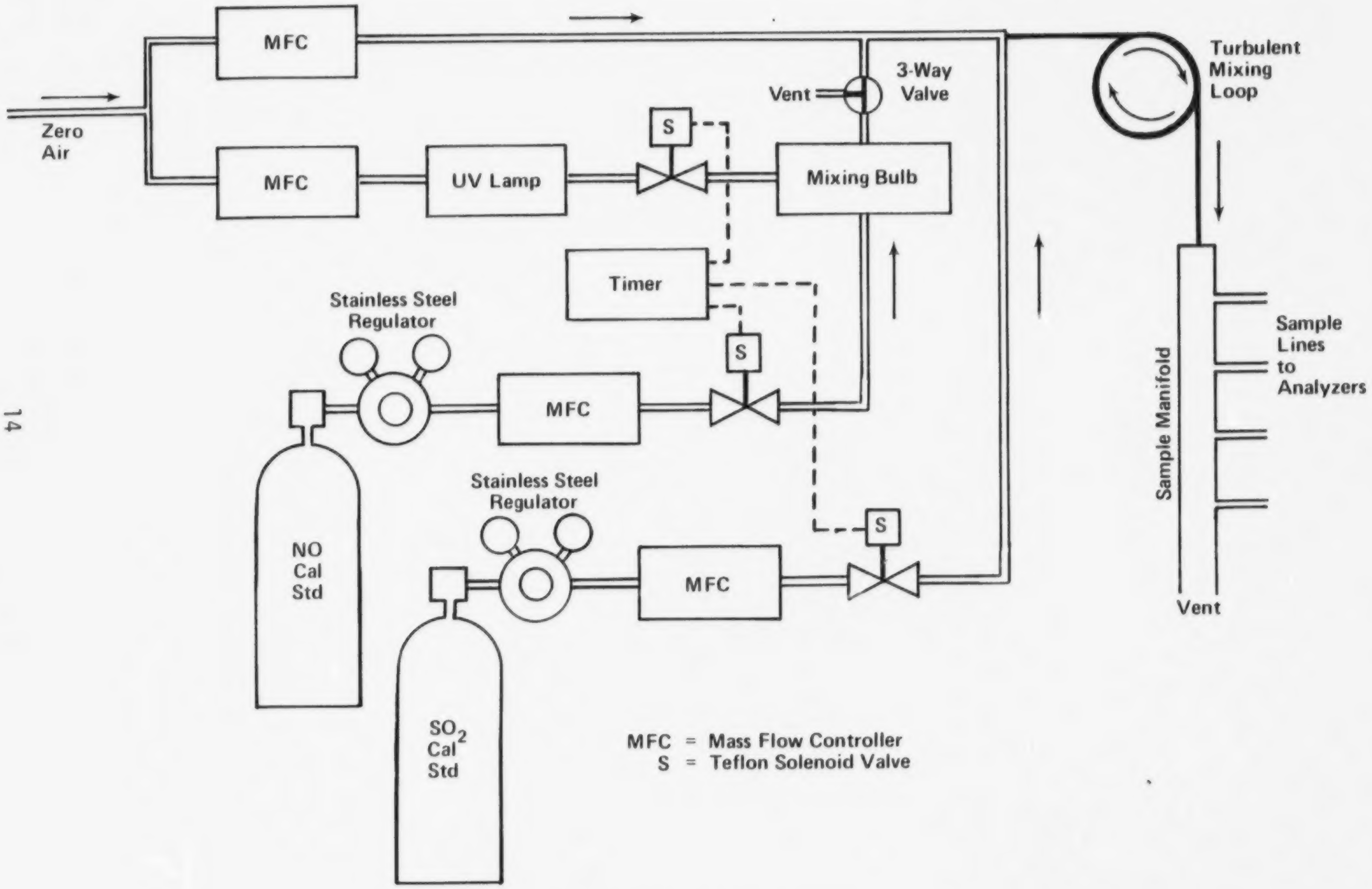
Zero Air
MFC
MFC
UV Lamp
S
Mixing Bulb
Vent
3-Way Valve
Timer
Stainless Steel Regulator
NO Cal Std
MFC
S
Stainless Steel Regulator
SO_2 Cal Std
MFC
S
Turbulent Mixing Loop
Sample Manifold
Sample Lines to Analyzers
Vent
MFC = Mass Flow Controller
S = Teflon Solenoid Valve

Figure 3. Field calibration apparatus.

Associated with the test manifold were the apparatus needed to generate sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), which are described in separate subsections below.

Sulfur Dioxide

Sulfur dioxide calibration standards and test mixtures were made by dynamic dilution with zero air of a cylinder of 0.83 ppm SO_2 and 350 ppm carbon dioxide (CO_2) in zero air, (analyzed by Scott-Marrin, Inc., Riverside, California) (Figure 2). The flow rates of both pollutant and diluent gases were controlled with mass flow controllers and verified daily with soap-film flowmeters. All surfaces were either stainless steel, PFA Teflon(TM), or PTFE Teflon(TM) and all surfaces from the mass flow controllers to the analyzer's sampling inlet were PFA Teflon(TM). Even with the use of relatively non-reactive PFA Teflon(TM) in the test manifold, sorption of SO_2 on the manifold surface may still have been a problem. Evidence suggesting a sorption problem was observed as a long stabilization time (approximately 2 hours) for each test day's initial change from zero to 80 percent full scale concentration for the analyzers. The analyzers quickly reached approximately 95 percent of their final, stable readings, but then only slowly reached their final, stable readings. It is assumed that the stabilization problem is associated with the manifold and not with the analyzer's internal surfaces. In addition, the determination of instrument response times may have been affected by the long manifold stabilization time. To reduce the time involved for each day's testing, the morning zero noise tests and the stabilization for the 80% calibration values were started by a digital timer before the laboratory personnel arrived on each test day. By the time the 80% precision measurements were performed, the manifold had been conditioned and the analyzer's responses had stabilized.

In addition to possible SO_2 losses in the manifold, the SO_2 may be lost in the pressure regulator. For this reason, a special electropolished, stainless steel pressure regulator with a Teflon(TM)-coated diaphram was purchased for this project and was used only with the SO_2 and NO calibration cylinders that were used in this project.

During the laboratory evaluation, the flow rates of dilution air and SO_2 were measured daily with a soap-film flowmeter. From these flow-rate measurements and the calibration standard's SO_2 concentration, the daily SO_2 calibration concentrations were calculated.

Nitrogen dioxide

Nitrogen dioxide was prepared by gas-phase titration of nitric oxide (NO) with ozone (O_3) (Figure 1). The NO was supplied from a cylinder of 5.35 ppm NO in nitrogen, (analyzed by Scott-Marrin, Inc., Riverside, California). The O_3 was produced by ultraviolet irradiation of zero air. The NO and O_3 were first mixed to produce NO_2 which was then diluted with zero air to form the test atmosphere. The flow rates of the NO, zero air used to produce O_3, and zero air used as diluent were controlled with mass flow controllers and verified with soap-film flowmeters on a daily basis.

The NO and O_3 must be allowed sufficient time to react to form NO_2 before the NO_2 is diluted to the final concentration. This was accomplished using a constant flow stirred tank reactor (CFSTR) fabricated from a Pyrex^{TM} flask and a magnetic stirrer. The reactor's volume was 510 milliliters (ml). The initial NO and O_3 concentrations were 5 and 4 ppm, respectively. Both the NO and the O_3 flow rates were 100 ml/min. Using these values and a rate constant of 24 ppm^{-1} min^{-1}, it is calculated that 98.5 percent of the O_3 has been reacted within the CFSTR (7, 8).

All surfaces downstream from the point at which NO and O_3 were mixed were made of PFA Teflon(TM). To reduce the time involved for each day's testing, the morning zero noise tests and the stabilization for the 80% calibration values were started by a digital timer before the laboratory personnel arrived on each test day. By the time the 80% precision measurements were performed, the manifold had been conditioned and the analyzer's responses had stabilized.

The same stainless steel pressure regulator purchased for use with the SO_2 calibration cylinder was used for the NO calibration cylinder. Pressure regulator losses for NO are much less than those for SO_2 (Jack Marrin, Scott-Marrin Co., personal communication, 1987).

Each day, the flow rates of dilution air, NO, and ozonator air were measured with a soap-film flowmeter. From these measurements, the NO and NO_x (i.e. NO plus NO_2) concentrations were calculated. The difference in the CSI 1600 analyzers' NO channel between measurements with and without the ozonator lamp covered was used to calculate the percent conversion of NO to NO_2. The average percent conversion of the two CSI 1600 analyzers was then multiplied by the NO_x concentration calculated from the measured flow rates to obtain the daily NO_2 concentration.

Whenever dynamic dilution is used to prepare gaseous calibration mixtures, the uncertainty of the final concentration is a function both of the uncertainty of the source gas concentration and of the uncertainty of the gas flow rates. For the NO_2 mixtures prepared in this study, an additional uncertainty arises due to the need to measure the percentage of NO converted to NO_2 by reaction with O_3. This additional uncertainty was reduced by using the average percent conversion taken from two independent measurements.

At the suggestion of Scintrex based on earlier testing in arid environments, the air for the laboratory NO_2 tests had a slight amount of water added to raise the relative humidity to between 10% and 30%. This was done by passing the dilution air over the surface of water in a sidearm flask. The calibration apparatus for the field evaluation did not humidify the calibration mixtures.

LABORATORY EVALUATION

Multi-Day Test Cycle

Guidelines for testing temperature and supply voltage variation dependencies have been established in the Code of Federal Regulations (2). These guidelines provide for varying the test temperature and voltage conditions in a seven-day test cycle during which the noise, precision, and drift tests are to be performed. If the analyzer fails any of these tests, an additional eight-day cycle is specified. As a result, the temperature and voltage test cycle may require fifteen days to complete.

Because the analyzers' performance parameters (rather than their ability to meet performance specifications) were being measured, there could be no failures and the nine-day cycle shown in Table 2 was used. This nine-day cycle provided duplicate measurements at each set of voltages and temperatures. To separate voltage and temperature effects from those of interferences, no interference testing was performed during these tests. During each day of the test cycle, the noise, precision, and drift tests (described below) were conducted as shown in the daily test sequence (Table 3).

Temperature and voltage control

The analyzers were tested in a temperature controlled environmental chamber (Sherer series CER controlled environment room). The temperature could be controlled to +/- 0.5 degrees Celsius over a range of 0 to 50 degrees Celsius. The line voltage for the analyzers was supplied from a dynamic line controller (California Instruments model LC-1201B) which supplied interference free, regulated 60-Hz power. The voltage was adjusted by use of a variable voltage AC transformer inserted between the analyzers and the dynamic line controller. This transformer permitted continious control of the analyzer supply voltage from 0 to 130 V AC with a regulation of +/- 1 V. The voltages and temperature were monitored by a Yellow Springs Instruments model 742-10 thermovolt thermometer and a AC-to-DC rectifier and were recorded on strip chart recorders (Hewlett Packard model 7132A and 7133A).

Data Acquisition

Data was acquired from the analyzer's voltage outputs by a Fluke 2240C data logger. This data logger permitted both instantaneous and time-averaged voltage measurements to be recorded. The printed output was manually entered into an IBM PC-XT (TM) microcomputer for processing using the Lotus 123 (TM) spreadsheet program. Hewlett Packard model 7132A and 7133A strip chart recorders were also connected to the analyzer outputs both to provide a permanent visual record of the analyzer output and to permit response time measurements (described below).

Precision

Precision is the ability of an analyzer to produce an uniform response for repeated measurements under identical conditions. The analyzer's precision is estimated by the standard deviation of a set of measurements at a uniform pollutant concentration. Two types of precision

TABLE 2. LINE VOLTAGE AND ROOM TEMPERATURE TEST CONDITIONS
(After Reference 2)

Test day	RMS Line Voltage[a] (Volts Ac)	Room Temperature[b] (Degrees Celsius)
0[c]	115	25
1	125	20
2	105	20
3	125	30
4	105	30
5	125	20
6	105	20
7	125	30
8	105	30

[a] Voltage specified shall be controlled to +/- 1 Volt.
[b] Temperature specified shall be controlled to +/- 1 degree Celsius.
[c] Setup and initial calibration occurred on Day 0.

Table 3. Daily Test Sequence for Laboratory Evaluation (Typical)

1) Noise and Zero Drift Test - measure 25 instantaneous readings of zero air at 2 min. intervals. The average of this is the morning (AM) zero value. The standard deviation is the noise at zero concentration.

2) NO measurement at 80% concentration (NO_2 analyzers only).

3) Precision and response time measurements at 80% concentration.

4) NO measurement at 50% concentration (NO_2 analyzers only).

5) Precision and response time measurements at 50% concentration.

6) Precision measurements at 20% concentration.

7) NO measurement at 20% concentration (NO_2 analyzers only).

8) Precision measurements at 0% concentration.

9) Noise and Zero Drift Test - measure 25 instantaneous readings of zero air at 2 min. intervals. The average of this is the evening (PM) zero value. The standard deviation is the noise at zero concentration.

estimates are commonly used, replication error and repeatability error. If the set of measurements are from a single sample, then their standard deviation is an estimate of the replication error of the analyzer. If the set of measurements are taken from different samples which have the same concentration, then the standard deviation is an estimate of the repeatability error of the analyzer. The repeatability error includes not only the replication error but also the variation caused by other components which may be present in the different samples (i.e. interference or matrix effects). Because synthetic test atmospheres do not have the same variation in interferents as is present in ambient air samples and because the concentration of ambient air samples is not controllable, the estimation of repeatability was not feasible in the laboratory or field evaluations. Thus, all laboratory precision estimates were for replication error. Although the variation due to interferents can not be directly evaluated, specific compounds were examined for their interference equivalents in separate laboratory tests (see below).

The analyzers' precision was measured throughout the range of concentrations comprising the calibration curve (i.e. at concentrations of zero, 20, 50, and 80 percent of the test range). The variation of precision with concentration can then be examined. In addition to the variation in response at a fixed concentration, there exists the possibility that an analyzer's response will be affected by previous measurements at either higher or lower concentrations (i.e. memory or hysteresis effects). To insure that this effect is included in the precision estimates, the equivalency specifications require that an analyzer be exposed to, alternately, zero air and a higher concentration of the test mixture between precision measurements. The evaluation of precision was similar to that described in reference 2, except that measurements were taken at additional concentrations specified above.

Noise

Noise, as defined in reference 2, is the standard deviation of twenty-five consecutive measurements of zero air taken at two minute intervals. The noise levels were measured both at the beginning and at the end of each daily session. Unlike the precision measurement at zero concentration described above, the noise measurement does not include the brief exposure to higher concentration samples. Noise measurements were not made at any other concentrations.

Detection Limit

Detection and quantitation limits were calculated from measurements of the analyzer's precision (rather than analyzer noise measurements). Lower detectable limits were calculated from the analyzer noise measurements.

A limit of detection (LOD) is defined as the minimum signal that may be distinguished from the background signal with a given confidence level. An LOD equal to three standard deviations of the signal for clean air is usually used (9). This represents the minimum signal which can be detected from the background with 93 percent confidence. The 0% precision values were used to calculate the LOD.

Since these analyzers are intended for use in quantitative (rather than qualitative) environmental measurements, simply detecting the presence or absence of a species is not adequate; a better criterion for a detection limit is the concentration at which the standard deviation is less than a given percentage of the species' concentration. This is referred to as the limit of quantitation (LOQ) and is generally taken as ten standard deviations at zero concentration (9). This value of the LOQ represents the concentration for which the standard deviation is 10 percent of the measured concentration (10). The 0% precision values were used to calculate the LOQ.

In summary, the LOD and LOQ are the minimum concentrations for which a given level of confidence in the measurement may be said to exist. The above calculations of the LOD and LOQ as multiples of the standard deviation assumes that the standard deviation is uniform across the measurement range. This is implied in the use of the 0% precision to establish confidence limits at the detection and quanitation limits. If the standard deviation increases with concentration, than the increased value of the standard deviation at the LOD and LOQ must be used.

A somewhat different approach to quantifying detection limits is used in the Code of Federal Regulations (2) which defines a lower detectable limit (LDL). This is specified as "the minimum pollutant concentration which produces a signal of twice the noise level" and a method is given for evaluating whether the LDL is below the performance specification of 10 ppb. This method is an acceptance test for high-level analyzers (0-500 ppb), but it is not suitable for extra-sensitive analyzers. For this reason, performance specifications for LDL described in reference 2 are not applicable for the extrasensitive analyzers. However, if it is assumed that the noise level is constant near the zero level, then the LDL may be estimated as twice the noise level at zero concentration.

It should be noted that the precision and noise estimates described in this section reflect replication error. Other errors such as between-instrument variability and sample matrix effects are not considered. Thus these precision, noise, LOD and LOQ estimates are a lower bound on their actual values.

Drift

The Code of Federal Regulations (2) specifies drift as the difference between two measurements taken at the beginning and end of the specified period. Drift measurements were made at zero concentration (12 and 24 hour periods) and at concentrations of 20, 50, and 80 percent of the instrument's upper range (24 hour periods). The 12-hour zero drift estimates were calculated as the difference between the means of the measurements of zero air at the beginning of daily testing and at the end of the previous test day. The 24-hour zero and span drift estimates were calculated as the difference between the mean of measurements at a given concentration on a given day and the those on the preceding day. Due to experimental considerations, it was not possible to perform these tests at exactly 12 and 24 hour intervals and the term "overnight drift" is used to indicate the drift between the beginning of a measurement session and the end of the previous day's session, while the term "daily drift" is used to indicate the drift between daily sessions. It should be noted that using these definitions of span drift, an analyzer which experiences zero drift will also experience span drift because the change in zero level will also be reflected in the span level.

In addition to this definition of drift, the equivalency specifications also define zero drift as the difference between the maximum and minimum values measured when sampling zero air over a 12 hour period. The use of maximum and minimum values as an estimate of drift was not used in this study because the data logger was turned off between the last noise measurement of one test day and the first noise measurement of the next test day.

Due to day-to-day variation in flow rates, it was not possible to produce exactly the same analyte concentration each day, except at zero concentration. The drift values for concentrations greater than zero have been corrected for variations in analyte concentration as calculated from daily flow measurements.

Daily Span Factor Drift

Another method for assessing the daily variation in instrument sensitivities is to examine the slope of the regressed line of analyte concentration (x-axis) versus instrument response (y-axis) for the four calibration mixtures at zero, 20, 50 and 80 percent of full-scale range. This slope is termed the "span factor" and tables of daily span factors and daily span factor drifts are given in the next section. The "daily span factor drift" is the percent difference between the span factors on two adjacent test days. Since the zero levels are factored out in the calculation of the slope, changes in the zero level (i.e. zero drift) will not affect the span factors.

Response Time

Response time is a parameter that describes the time it takes the analyzer to respond to a change in pollutant concentration. Analyzer response time is estimated by three test parameters: lag time, rise time, and fall time. In this project, rise time and fall time were measured from the analyzers' strip chart recorder traces. The lag time was not measured. Rise and fall times are measured by the following procedure:

1) Sample zero air until a stable analyzer reading has been obtained. Concurrently, an air stream containing the pollutant of interest is being vented through the 3-way valve in the calibration apparatus.
2) Turn the 3-way valve to produce a step concentration change in the sample airstream. The time between the step concentration change and the initial analyzer response to the change is the lag time. The extrasensitive analyzers' lag times were not measured in this project.
3) Sample the airstream until a stable upscale analyzer reading has been observed on the strip chart trace. Measure, on the strip chart, the difference between the time of initial analyzer response and the time of 95 percent of the stable upscale analyzer reading. This difference is the analyzer's rise time.

4) Turn the 3-way value back to the vent position to produce another step concentration change. Sample zero air until a stable analyzer reading has been reestablished. Measure, on the strip chart, the difference between the last time of a stable upscale analyzer reading and the time of 5 percent of the stable upscale analyzer reading. This difference is the analyzer's fall time.

This procedure was to be performed three times each day of the test cycle. On most days, this procedure was combined with the 80 percent precision test, above.

Interferences

Purpose of interference testing --

The interference tests were performed to obtain a quantitative estimate of the extrasensitive analyzers' responses to several potential interferents. They were typically performed at interferent concentrations that are greatly in excess of those expected in ambient air. This approach was chosen for three reasons. First, generation of many interferents at the low concentrations seen in ambient air would have posed considerable difficulties both in possible manifold sorption and in measurement of the interferent concentrations. Second, the ambient concentrations of many interferents are either not well known or highly variable. This makes the selection of a representative interferent level for the interference tests somewhat subjective, especially in the absence of performance specifications for these analyzers. Third, the instrument response to the interferent may be difficult to quantify at low interferent concentrations.

The results of the interference tests are presented as relative interference responses in units of ppb analyzer response/ppb interferent. The relative interferent response factors out the interferent concentration from the test results. By measuring the relative interferent response at higher concentrations not only are the experimental difficulties reduced and better quantitation obtained, but the analyzers' responses at lower interferent concentrations may be estimated by multiplying the ambient interferent concentration by the relative interferent response.

In general, the interference tests were performed in the presence of the species of interest (i.e. NO_2 and SO_2) at a concentration equal to 50 percent of the analyzer's full scale test range. Each interferent was tested individually.

Although the results of the interference tests had not been intended to be used to correct data obtained during the field evaluation, one exception was made. The NO relative interference responses for the TECO 43S SO_2 analyzers were used with measured NO concentrations from the CSI 1600 NO_2 analyzers to obtain corrected SO_2 concentrations for the TECO 43S SO_2 analyzers. This correction was necessary because relatively large NO concentrations (i.e. greater than 50 ppb) were measured during the field evaluation.

Selection of interferents for testing --

Any chemical compound which produces a response in or change of response in the analyzer is an interferent. The compounds tested were those that are either widely present in the atmosphere, known to interfere from previous studies on instruments employing the same measurement principle, or thought likely to interfere based on the analyzer's detection principle. Since the interference may be due to a quenching of pollutant response rather than a direct response to the interferent, interferents were mixed the pollutant species for the interference testing where practical.

Widely occurring compounds which may interfere include water vapor (H_2O), CO_2, and oxygen (O_2). These compounds are known to quench various fluorescent and photochemical processes. Since all of the analyzers to be tested were either fluorescence or chemiluminescence analyzers, these compounds were tested for all analyzers.

Sulfur dioxide analyzers using UVF as their measurement principle may be subject to quenching interference from H_2O, CO_2, and O_2 variation (11-14). They are also subject to interference from species which fluoresce in the same spectral region as SO_2, such as the aromatic hydrocarbon xylene (C_8H_{10}) (15). Although designated equivalent UVF SO_2 analyzers have overcome these interferences for compliance monitoring (16), testing was performed to verify that no interferences exist for the extrasensitive version of this instrument. The Code of Federal Regulations (2) specifies testing ammonia (NH_3), NO, SO_2, and H_2O as interferents for NO_2 analyzers using the chemiluminescent reaction with ozone (e.g. the CSI 1600). In addition, interference has been observed from peroxyacetyl nitrate (PAN), nitric acid (HNO_3), organic nitrates, and ethyl nitrite (17).

Nitrogen dioxide analyzers based on luminol chemiluminescence, such as the LMA 3 analyzer, have been reported to suffer interferences due to oxidizing species such as O_3, SO_2, and acidic species such as CO_2 (4 and 5). In addition, interference from PAN has been reported (18 and 19). Additionally, the LMA 3 analyzers were tested for their relative response to ammonia (NH_3), hydrogen chloride (HCl) and nitrous acid (HNO_2). The analyzers were not tested for hydrogen peroxide interference. The LMA 3 analyzers were tested with the O_3 traps supplied by Scintrex.

Test interferent concentrations were selected in general to exceed that which could be seen in the ambient air. However, H_2O can be found in the ambient air at concentrations as high as 100 percent relative humidity. Testing with 100 percent relative humidity could result in condensation within the test manifold from small temperature fluctuations and could also result in long stabilization times. For these reasons, water interference was tested at approximately 50 percent relative humidity.

Generation of interferents --

Since interferent concentrations were several orders of magnitude greater than the pollutant concentration, the relative sorption losses for the interferents in the test manifold were less than those for the pollutants. The resultant mixture was then mixed with the pollutant gas in a PFA Teflon(TM) mixing tee and delivered in a PFA Teflon(TM) test manifold (as above). This procedure ensured that the dilute pollutant gas only contacted PFA Teflon(TM) surfaces.

Water vapor (H_2O) --

Water vapor was generated by passing dry zero air through a humidifying chamber filled with water. The water concentration was measured with an EG + G model 660 dew-point hydrometer connected to the sampling manifold.

Nitric oxide (NO) and nitrogen dioxide (NO_2) --

NO and NO_2 were generated as described under Nitrogen Dioxide above. Because cylinders of NO often contain trace amounts of NO_2 which would cause a response on NO_2 analyzers, NO interferent testing of the NO_2 analyzers was not performed. However, during the NO measurements performed as part of the daily test cycle (see Table 3, above), the LMA 3 analyzers' response at 80% NO concentration was well under 1% of full scale response. This response may reasonably be attributed to NO_2 present in the NO cylinder.

Sulfur dioxide (SO_2) --

Sulfur dioxide interferent test mixtures were made by dynamic dilution of a cylinder of 46.3 ppm SO_2 in nitrogen with zero air. The flow rates of interferent, pollutant, and diluent gases were controlled with mass flow controllers and verified with soap-film flowmeters.

Carbon dioxide (CO_2) --

Carbon dioxide interferent test mixtures were made by dynamic dilution of a cylinder of 11.6 percent CO_2 in nitrogen with zero air. The concentration of this cylinder has previously been verified in another project. The concentration of the CO_2 at the manifold was not verified. The flow rates of interferent, pollutant, and diluent gases were controlled with mass flow controllers and verified with soap-film flowmeters.

Oxygen (O_2) --

Oxygen is an effective quencher of many photochemical reactions. The effect of varying O_2 concentrations on analyzer sensitivity was examined by analyzing a test atmosphere prepared using nitrogen rather than zero air (approximately 21 percent O_2) as the diluent gas. In addition, a cylinder of 37 percent O_2 in N_2 was used as the dilutant gas to test enriched O_2 concentrations. The oxygen concentration in the manifold was not verified.

Ozone (O_3) --

Ozone was generated by ultraviolet irradiation of zero air. The O_3 concentration was verified with a Bendix model 8002 O_3 analyzer calibrated by gas-phase titration with NO (See Nitrogen Dioxide above). The ozone interference tests for the LMA 3 analyzers were performed with the ozone traps supplied by Scintrex. Because O_3 reacts with NO_2 to form other nitrogen oxides, NO_2 was not present during the O_3 interference test.

Nitric Acid (HNO_3) --

Nitric acid was generated from a gravimetrically calibrated permeation tube. The concentration was verified at the test manifold by sampling through Nylasorb(TM) filters to collect HNO_3. The collected HNO_3 was desorbed in 0.003N NaOH and the resulting extract was analyzed for its nitrate concentration by ion chromatography. NO_2 was not present during the interferent tests. Because HNO_3 tends to sorb on the surfaces of the test manifold, the manifold was allowed to equilibrate overnight before the HNO_3 interference measurements were recorded. The HNO_3 interference tests were performed at the end of the laboratory evaluation to avoid the possibility that residual HNO_3 desorbing from the manifold might affect subsequent tests.

PFA Teflon(TM) tubing has been found to be superior to TFE or FEP Teflon(TM) tubing in its HNO_3 transmission characteristics (20).

Peroxyacetyl Nitrite (PAN) --

Peroxyacetyl nitrate poses particular difficulties due to its lack of stability. Calibration is difficult since liquid PAN is subject to decomposition with the possibility of spontaneous explosion (21). For this reason, PAN was generated in a dilute solution of iso-octane by the method of Holdren and Spicer (22). This solution was evaporated in Tedlar(TM) bags which were sampled for the interference tests. To prevent decomposition of PAN, NO_2 was added to the sample bags. The PAN interference was taken as the difference between the analyzer response with PAN and NO_2 and with only NO_2 present. PAN concentrations were determined by assuming that the CSI 1600 NO_2 analyzer has nearly quanitative response to PAN (23). Accordingly, only the LMA 3 analyzers was tested for PAN interference, while the CSI 1600 analyzers were used to estimate the amount of PAN present.

Xylene (C_8H_{10}) --

Xylene was generated by dynamic dilution of a cylinder of 344 ppm metaxylene, $((CH_3)_2C_6H_4)$, in nitrogen. The cylinder concentration had previously been verified, in another RTI project, against NBS benzene SRMs by gas chromatography using a flame ionization detector. The manifold concentration was not verified.

Hydrogen Chloride (HCl) --

Hydrogen chloride was generated by dynamic dilution of a cylinder of 56.6 ppm HCl in nitrogen with zero air. The cylinder concentration was verified as part of another RTI project. The manifold concentration was not verified.

Ammonia (NH_3) --

Ammonia was generated by dynamic dilution of a cylinder of 80.6 ppm NH_3 in nitrogen. NO_2 was not present during the NH_3 interference test. Our original intention was to verify the manifold concentration by collection on citric acid-coated filters as NH_4^+ followed by extraction of the filters with water and colorimetric analysis. The interference test was performed and approximately 2 hours were allowed for filter loading. During this period, the NO_2 analyzers showed the same response as to zero air. At the end of this time, the filters were removed. Subsequent analysis of the citric acid-coated filters, showed no NH_3 present. After the filters were removed, a rise in NO_2 was seen on the CSI 1600 analyzer nearest to the beginning of the manifold. Subsequently, response was seen on both CSI 1600 analyzers and a TECO 14 B/E NO_2 analyzer which was also sampling at the far end of the manifold. After waiting an additional 1.5 hours for a level response, analyzer voltage measurements were made. It is believed that the long time for analyzer response to NH_3 reflects sorption on the manifold walls.

Nitrous Acid (HNO_2) --

Nitrous acid (HNO_2) interference tests were performed on the NO_2 analyzers at the end of the field evaluation. HNO_2 was generated by use of a sublimation generator similar to that used by Braman and de la Cantera (24). Unfortunately, this generator is not very stable in output. Due to the long time required for filter loading and the instability of the generator, verification of the HNO_2 concentration by filter samples was not attempted. It was assumed that the CSI 1600 analyzers had a quantitative response to HNO_2 and the CSI 1600 analyzers' response was taken as the HNO_2 concentration. The LMA 3 analyzers' response was then measured relative to that of the CSI 1600 analyzer. No NO_2 was added during the interference test.

The generator may also produce small amounts of NO, NO_2, and HNO_3. A nylon filter was placed on the generator output to collect any HNO_3 that might be present. Measurements of NO_2 response were made with and without an Na_2CO_3-coated filter present on the generator output, which collects HNO_2 but has poor collection efficiencies for NO and NO_2. The difference between these two measurements represents the analyzer's response to HNO_2 as NO_2. The two LMA 3 analyzers saw 37% and 54% of the average CSI 1600 analyzers' response (for LMA A and LMA B respectively).

Hydrogen Sulfide --

Hydrogen sulfide (H_2S) was generated by dynamic dilution of a cylinder containing 30 ppm of H_2S in nitrogen. It should be noted that that a trace amount of SO_2 could have been present in the H_2S cylinder due to possible oxidation of H_2S. The interference measured thus is an upper bound on the actual interference due to H_2S. The concentration of H_2S in the manifold was not verified.

FIELD EVALUATION

Site Description

The field evaluation was performed at the RTI Materials Exposure Site, which is located on the RTI campus in Research Triangle Park, NC (see Figure 4). The site is a grassy, open 2.4 hectare area located near a divided, limited-access highway. The extrasensitive analyzers were located in a 2.4 meters x 10.7 meters mobile laboratory/monitoring trailer at the center of this site. Continuous monitors for several air pollutants (Table 4) and meteorlogical parameters are also operated in in this trailer in conjunction with other RTI projects. The data from selected analyzers was also taken by the data acquisition system described below. The extrasensitive analyzers were operated from April 26 through May 27, 1988 (i.e., Julian days 117 through 147) at the RTI Materials Exposure Site.

Sample Manifold

The manifold that was used for ambient air sampling is made of 3.2-centimeter OD (2.7-centimeter ID) borosilicate glass tubing. The manifold inlet is an inverted 15-centimeter diameter, glass funnel which provides protection against rain entering the manifold. This inlet is

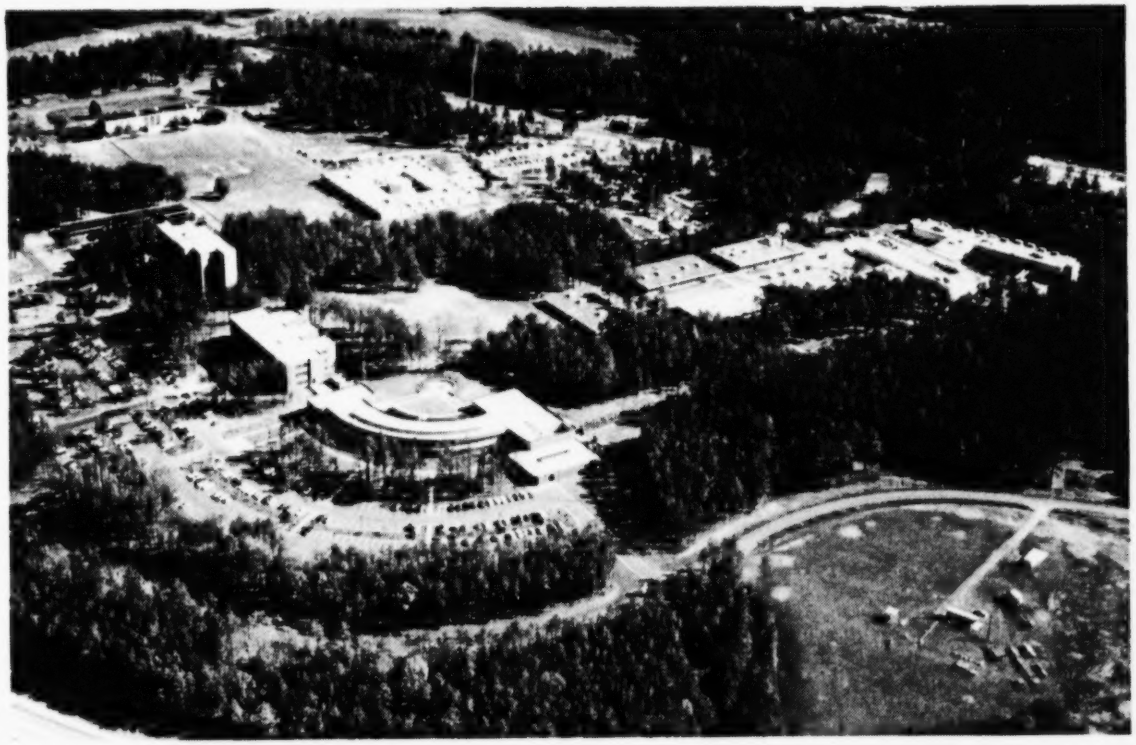

Figure 4. Research Triangle Institute with Materials Exposure Site in the Lower Right corner.

TABLE 4. AMBIENT AIR ANALYZERS AND METEOROLOGICAL INSTRUMENTS AT RTI MATERIALS EXPOSURE SITE

Species	Manufacturer	Model	Range Used
SO_2	Thermo Environmental	43A	0 to 200 ppb
NO, NO_x	Bendix	8101	0 to 500 ppb
O_3	Bendix	8002	0 to 500 ppb
Dew Point	Climatronics	EWS	-40 to 20°C
Wind Direction	Climatronics	EWS	0 to 360°
Wind Speed	Climatronics	EWS	0 to 25 m/s
Temperature	Climatronics	EWS	0 to 50°C
Solar Radiation	Climatronics	EWS	0 to 200 Ly

attached to an approximately 2.4-meter long, vertical section of glass tubing which is mounted to the outside of the trailer. This section is connected via a glass tee joint and a bug collection bottle to a horizontal section of glass tubing which is mounted inside the trailer.

The extrasensitive analyzers' sample lines are connected to the horizontal section at a distance of approximately 2.7 meters downstream of the tee joint. The connectors are 0.6-centimeter glass ball joints. The other ambient air quality analyzers' sample lines are connected to the manifold at a distance of approximately 5.2 meters further downstream. Their connectors are also 0.6-centimeter glass ball joints.

Ambient air is pulled through the manifold by a squirrel-cage blower that is located at the far end of the manifold. The manifold exhaust is at the far end of the trailer. The pressure drop across the manifold is approximately 1-centimeter H_2O (or less than 1 millimeter Hg).

Data Acquisition

The recorder output of each analyzer was attached to a Fluke Helios data acquisition system which was operated by a Tandy 3000 computer. Voltage data from the extrasensitive analyzers was sampled every 2 minutes and stored on disk for later processing by a DEC VAX computer. Voltage resolution was 1mV. This corresponds to a concentration resolution of 0.001 ppb for the TECO 43S analyzers, 0.010 ppb for the LMA 3 analyzers, and 0.050 ppb for the CSI 1600 analyzers. The station analyzers had a concentration resolution of 0.020 ppb for the TECO 43A SO_2 analyzer and 0.500 ppb for the other ambient air monitors. The recorder outputs were also connected to strip chart recorders (Hewlett Packard models 7132A and 7133A) to provide a immediate and permanent visual record of instrument levels.

Data Processing

Throughout the field evaluation, data from the extrasensitive analyzers were transferred from the Tandy computer to the VAX computer. At the end of the field evaluation, these data were processed as is described in the following paragraphs. A flow chart of the overall data handling system is given in Figure 5.

The data handling programs which were used in the current study are designed to maximize the use of calibration information while minimizing manual calculation and data manipulation. This approach helps insure the validity of the reported data. The calculation of parameter concentrations from the raw data is made possible by calibration subroutines in the programs. In addition to the advantages of storing the data in the rawest possible state, this also permits the calibration information to be modified without alteration of the data itself.

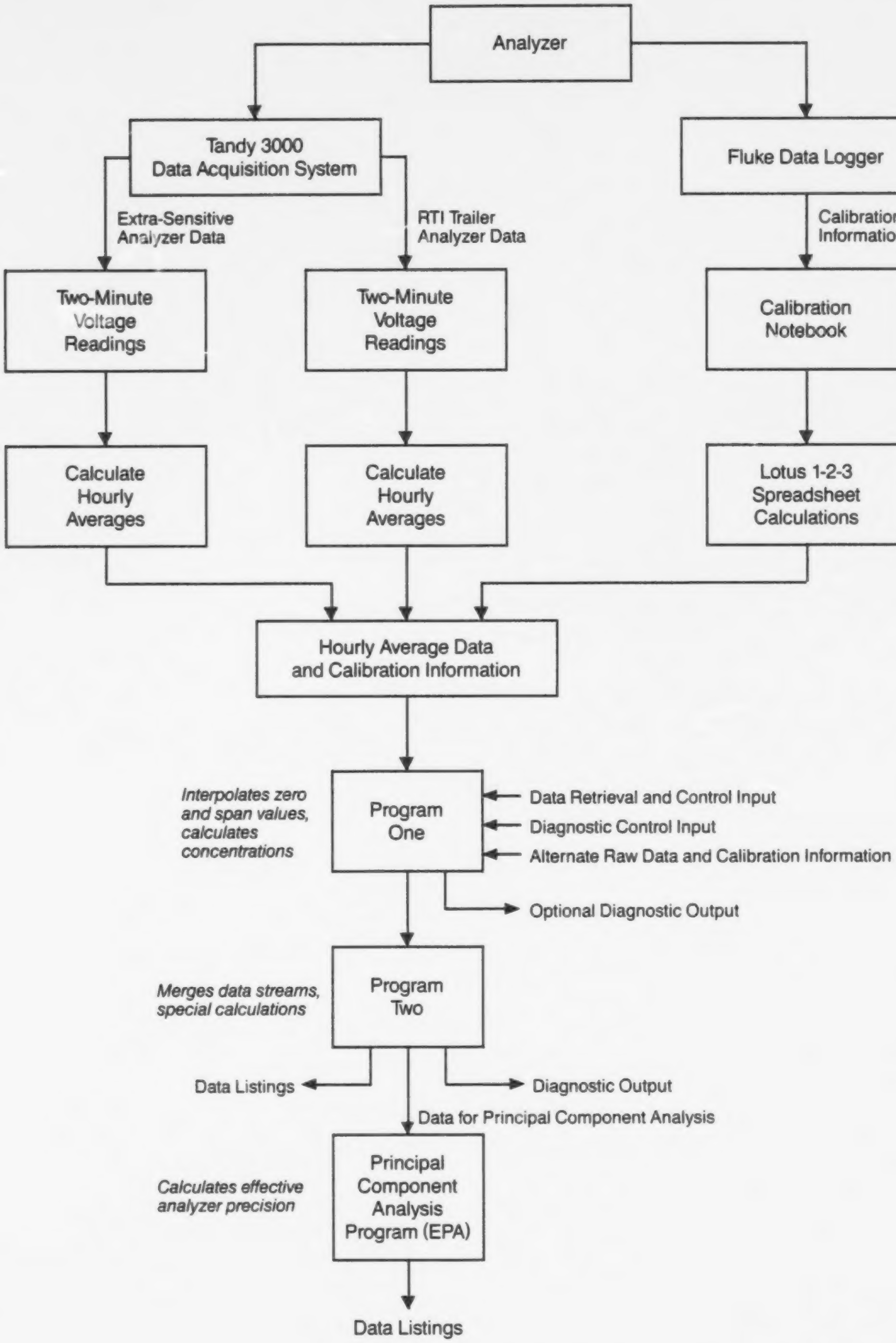
Analyzer
Tandy 3000 Data Acquisition System
Fluke Data Logger
Extra-Sensitive Analyzer Data
RTI Trailer Analyzer Data
Calibration Information
Two-Minute Voltage Readings
Two-Minute Voltage Readings
Calibration Notebook
Calculate Hourly Averages
Calculate Hourly Averages
Lotus 1-2-3 Spreadsheet Calculations
Hourly Average Data and Calibration Information
Interpolates zero and span values, calculates concentrations
Program One
Data Retrieval and Control Input
Diagnostic Control Input
Alternate Raw Data and Calibration Information
Optional Diagnostic Output
Merges data streams, special calculations
Program Two
Data Listings
Diagnostic Output
Data for Principal Component Analysis
Calculates effective analyzer precision
Principal Component Analysis Program (EPA)
Data Listings

Figure 5. Flowchart of overall data handling system.

The first step in the process is to convert the 2-minute instantaneous voltage readings into hourly average voltages. The two-minute readings are checked to insure that they do not exceed the following overrange limits:

Analyzer	Overrange Limit
LMA 3	5.0 volts
CSI 1600	1.3 volts
TECO 43S	11.3 volts

Overranged readings are not included in the hourly average voltages. Hourly averages containing more than 25 percent overranged readings are discarded. Values of 999 volts are inserted in their place to indicate missing data. Two-minute readings are also discarded when the data acquisition system's calibration flag is high. Values of 999 volts are inserted in their place to indicate missing data.

The data are processed in groups of four parameters (e.g. the two TECO 43S analyzers and the two CSI 1600 analyzers), rather than as individual parameters or as the entire ensemble of parameters. The hourly averages are divided into groups of two or three whole days containing up to fifty hourly averages. Zero and span factors are manually inserted into the hourly averages at the appropriate times. The zero and span factors are used in the next step to calculate the pollutant concentrations. An unique identification number (based on the SAROAD parameter codes) for each analyzer/pollutant combination is manually inserted at the beginning of each group of hourly averages.

The data for the trailer analyzers are processed in a similar manner, but separately. At this point in the process, the trailer analyzer data are appended to the extrasensitive analyzer data.

In the next step in the process, Program One converts the hourly average voltages into hourly average concentrations. The first step in Program One is to calculate zero and span values for each measurement. Since the analyzers' zero and span factors shift from one day to the next, error would result if fixed zero and span factors were used for each day. This problem is avoided by the calculation of linearly interpolated zero and span factored between the times of the zero and span checks. These interpolated calibration values are then used to convert the measurements to concentration units. In addition to employing routine zero-and-span type calibrations, Program One has the capability of handling more complex nonlinear calibration calculations and data validity assessments via special algorithms, which are tailored to individual parameters. Program One also converts the times associated with each group of measurements from hours and minutes to decimal hours (EST). At this stage, the hourly average concentrations are still separated into groups of up to four parameters. The data are put in chronological order within each parameter group and are ready to pass through to Program Two.

The main purpose of Program Two is to further organize the hourly average concentration such that all the measurements for a particular time are merged into a single ensemble. Program Two also performs special calculations which involve measurements from different parameters. Examples of this feature are the calculation of concentration differences between the two extrasensitive analyzers in each analyzer model, the calculation of the average NO concentration from the two CSI 1600 analyzers and the calculation of corrected TECO 43S SO_2 concentrations which remove the nitric oxide interference. The latter calculations use the following formulas:

$$\text{corrected TECO A } [SO_2] = \text{measured } [SO_2] - \left[\frac{\text{average } [NO]}{36.3111}\right]$$

$$\text{corrected TECO B } [SO_2] = \text{measured } [SO_2] - \left[\frac{\text{average } [NO]}{46.7463}\right]$$

where 36.311 and 46.7463 are reciprocals of the relative interference responses to NO that were measured during the laboratory evaluation. The final step in Program Two is to list the data in an organized fashion with appropriate header information. The data contain blank spaces that designate missing data. Values of 0 ppb or less are listed as 0.0000. The header labels are explained in Table 5.

In addition to producing a listing of the hourly average concentrations, both programs provide detailed diagnostic data listings of intermediate calculations to facilitate verification and correction of the data. In the present study, both programs were run at least twice. Initially, listings were generated to facilitate verification and correction of the data. After review of the data, the final listings were produced and may be obtained by written request to the authors.

Calibration

In addition to the data aquisition system used to record field data, a Fluke model 2240C data logger was attached to the output of each extrasensitive analyzer to provide time-averaged measurements for calibration purposes. Several instantaneous voltage readings by the data logger were compared to those of the Fluke Helios system described above to ensure that there was no bias between the calibration data logger and the station data acquisition system.

Zero and 80% span values were taken daily between April 26 and May 12, 1988 and once every two days between May 12 and 26, 1988. The calibration data from the field evaluation was compared to the corresponding values that were obtained from the laboratory evaluation. Daily fluctuations in zero and spans appeared similar to those during the laboratory evaluation. This similarity indicated that the analyzers were functioning properly in the field evaluation and thus, the frequency of zero and span values was reduced to every other day for the rest of the field evaluation.

TABLE 5. DESCRIPTION OF HEADER LABELS FOR AMBIENT AIR QUALITY MEASUREMENTS

Parameter Name	Parameter Units	Parameter Description
RTI-SO_2	ppb	Sulfur dioxide from trailer TECO 43A instrument
RTI-O_3	ppb	Ozone from trailer instrument
RTI-NO	ppb	Nitric oxide from trailer instrument
RTI-NO_2[a]	ppb	Nitrogen dioxide from trailer instrument
RTI-NO_x	ppb	Nitrogen oxides from trailer instrument
TEMP	RC	Ambient air temperature from trailer instrument
DEWPT	RC	Ambient air dewpoint from trailer instrument
REL HUM[a]	%	Percent relative humidity from trailer instrument
TSR	LY/Hour	Total solar radiation from trailer instrument
TA-SO_2	ppb	Uncorrected sulfur dioxide from TECO 43S (A) instrument
TB-SO_2	ppb	Uncorrected sulfur dioxide from TECO 43S (B) instrument
LA-NO_2	ppb	Nitrogen dioxide from Scintrex LMA-3 (A) instrument
LB-NO_2	ppb	Nitrogen dioxide from Scintrex LMA-3 (B) instrument
CA-NO	ppb	Nitric oxide from CSI 1600 (A) instrument
CA-NO_2	ppb	Nitrogen dioxide from CSI 1600 (A) instrument
CA-NO_x	ppb	Nitrogen oxides from CSI 1600 (A) instrument
CB-NO	ppb	Nitric oxide from CSI 1600 (B) instrument
CB-NO_2	ppb	Nitrogen dioxide from CSI 1600 (B) instrument
CB-NO_x	ppb	Nitrogen oxides from CSI 1600 (B) instrument

[a] This parameter is calculated by the data processing program from other input parameters.

(Continued)

TABLE 5. DESCRIPTION OF HEADER LABELS FOR AMBIENT AIR QUALITY MEASUREMENTS (Cont'd)

Parameter Name	Parameter Units	Parameter Description
COR-43SA[a]	ppb	Corrected sulfur dioxide from TECO 43S(A) instrument
COR-43SB[a]	ppb	Corrected sulfur dioxide from TECO 43S(B) instrument
TD-SO_2[a]	ppb	Difference between corrected sulfur dioxide values from TECO 43S instruments
LD-NO_2[a]	ppb	Difference between nitrogen dioxide values Scintrex LMA-3 instruments
CD-NO[a]	ppb	Difference between nitric oxide values from CSI 1600 instruments
CD-NO_2[a]	ppb	Difference between nitrogen dioxide values from CSI 1600 instruments
CD-NO_x	ppb	Difference between nitrogen oxides valus from CSI 1600 instruments
AVG-NO	ppb	Average nitric oxide value from CSI 1600 instruments

[a] This parameter is calculated by the data processing program from other input parameters.

The field calibration of extrasensitive analyzers was performed using the same manifold·used for the laboratory evaluation. After calibration, the analyzers were manually reconnected to the station manifold for ambient air sampling. The station analyzers were connected through two way solenoids both to a separate calibration manifold and to the sampling manifold. An automatic calibration controller was used to perform the calibration valve switching sequence for the station instruments.

To reduce the calibration time, calibration of the NO_2 analyzers and SO_2 analyzers was conducted simultaneously. This was done by combining the laboratory NO_2 and SO_2 generation apparatus as shown in Figure 3. Since NO was present in the combined calibration mixture, it was necessary to use the average NO levels measured by the CSI 1600 analyzers and the relative interference response measured in the laboratory interference tests to correct the TECO 43S analyzers' span factors. In addition, to reduce the time spent waiting for equilibration, the flow through the calibration manifold was started by a digital timer several hours before the calibration . Otherwise the generation procedures were similar to those employed in the laboratory evaluation.

Since the field monitoring site was near a major highway, ambient NO levels in excess of 50 ppb were occasionally measured. This produced noticeable interference levels on the TECO 43S SO_2 analyzers. To correct for this, the same procedure used to correct the calibration data was also used to compensate for NO interference in ambient air samples.

Principal Component Analysis

One of the difficulties in a field comparison of different analyzers is the absence of any standard or analyzer which can be used as a reference for comparison of the various analyzers. In a laboratory comparison, the concentration calculated from the source gas and dilution rates may be used as the reference standard, but in a field evaluation the actual (as opposed to the measured) concentration is not known. Thus it becomes necessary to provide a surrogate concentration for use as a reference. Holland and McElroy describe the use of principal component analysis (PCA) as a means of providing a reference concentration to obtain an estimate of the effective operating precision and detection limits of several gas-phase chemiluminescent NO_2 analyzers (25). Here the reference concentration is taken as a linear combination of the concentrations measured by all of the independent analyzers. The coefficients of the concentrations are calculated in a manner similar to least-squares regression (26 and 28). Using PCA, each measured value can be compared to the calculated reference value and an estimate of effective operating precision obtained.

With the assistance of D. M. Holland of EPA, we used his program running on EPA's Sperry UNIVAC 1100 computer system to perform a PCA analysis of precision of the field evaluation data for the NO_2 analyzers. The precisions of the SO_2 analyzers in the field evaluation were determined using a similar PCA program that was written and run at RTI.

SECTION 5
TEST RESULTS

IDENTIFICATION OF ANALYZERS

The test results from the laboratory and field evaluations of the sulfur dioxide and nitrogen dioxide extrasensitive analyzers are summarized in the following pages. To simplify the identification of analyzers, the identifiers shown in Table 6 are used.

TABLE 6. INSTRUMENT IDENTIFIERS USED IN LABORATORY AND FIELD EVALUATION

Identifier	Analyzer	Species	Serial number	EPA property no.
LMA A	Scintrex LMA 3	NO_2	8708187	814042
LMA B	Scintrex LMA 3	NO_2	8708185	814041
CSI A	CSI 1600	NO_2	12815	814145
CSI B	CSI 1600	NO_2	12814	814146
TECO A	TECO 43S	SO_2	43S-22818-207	883918
TECO B	TECO 43S	SO_2	43S-22817-207	883919

LABORATORY EVALUATION OF NITROGEN DIOXIDE ANALYZERS

Maintenance and Operational Failures

The CSI 1600 NO_2 analyzers required replacement of the dessicant (Drierite™) used to dry the ozonator intake line. This is considered normal maintenance for this model. Starting on day zero, one of the two LMA 3 NO_2 analyzers (LMA B) experienced problems with luminol solution being sucked out of the cell and into the dropout trap. When the dropout trap overflowed, fluid went into the hydrophobic air pump filter, greatly reducing air flow. A small amount of luminol was sucked into the air flow capillary used to limit air flow and into the air pump intake line. Cleaning the trap and replacing the air filter did not stop the fluid from being sucked out of the cell but did restore normal air flow, permitting analyzer operation. Replacement of the air filter was necessary because the dried luminol solution clogged the filter which restricted air flow. A temporary solution to the overflow problem was obtained by replacing the factory installed dropout trap (volume approximately 5 mL) with a midget impinger (volume of approximately 25 to 30 mL capacity). This replacement extended the time of operation between trap overflows to the point that a daily draining of the trap was sufficient to prevent an overflow. After some trial and error and consultation with factory representatives, the pump tubing on both entrance and exit sides of the pump was replaced (this was on the second day of the interference tests). Visual inspection of the used pump tubing showed noticeable wear. Tubing replacement improved the ability of the pump to remove liquid from the cell and greatly reduced the amount of fluid sucked into the air line. After a gentle bending of the bracket which holds and tensions the pump tubing, the problem with trap overflow disappeared. After this problem, it was decided to replace pump tubing at approximately 2-week intervals for the duration of lab and field evaluations. Since this interval was approximately the length of time in which the LMA 3 analyzers emptied their luminol reservoir (1-liter capacity), it was convenient to simply replace the pump tubing when the reservoirs were refilled as part of normal maintenance.

In addition to the problem with trap overflow on LMA B, both LMA 3 analyzers experienced an increase in noise and in zero levels after several days of operation without being backflushed. Several cycles of backflushing the cell with deionized water restored normal operation. It is hypothesized that the increase in noise is due to clogging of the cell wick and porous reaction areas with dried luminol solution, which is washed out with the backflush of deionized water. Based on this experience during the laboratory evaluation, a daily backflushing was performed during the field evaluation. This is easily done by pressing a switch located on the instrument front panel, which initiates an automatic backflush cycle. A remote connector is provided on the rear panel for use with an automatic timer (this feature was not used in this project). It should be noted that the term "backflush" is actually a misnomer for current LMA 3 models as the deionized water wash is actually pumped through the cell in the normal direction (Janice Green, Scintrex Ltd., personal communication).

In summary, although problems were experienced with the LMA 3 analyzers, it is felt, with hindsight, that most problems could have been avoided if the analyzers were backflushed daily, if their pump tubing were replaced every two weeks (i.e. with each solution replenishment) and if the pump tensioning bracket in LMA B had been properly aligned. For this reason, it is strongly recommended that a regular schedule of backflushing and tubing replacement be incorporated at all sites using the LMA 3 analyzer.

Noise

Noise measurements, at zero concentration, are shown in Table 7. The LMA 3 analyzers had lower noise values than the CSI 1600 analyzers. Within a single analyzer model, the noise values were generally consistent. This consistency was seen between the two analyzers of each model, across the nine test days and between the morning and evening zero drift tests.

Precision

Precision measurements, expressed as the standard deviation of repeated measurements, indicate better precision (i.e. lower precision values) for the LMA 3 analyzers as compared to the CSI 1600 analyzer (Table 8). Precision measurements were made at zero, 20, 50 and 80 percent of each analyzer's full-scale range. Within a single analyzer model, the precision values were generally consistent. This consistency was seen between the two analyzers of each model and across the nine test days. A qualitative review of the precision data suggests that the precision varied

TABLE 7. NOISE MEASUREMENTS FOR NITROGEN DIOXIDE ANALYZERS

	Standard deviation (ppb) during morning zero drift tests			
Day	LMA A	LMA B	CSI A	CSI B
0	0.0025	0.0015	0.270	0.375
1	0.0010	0.0007	0.342	0.330
2	0.0049	0.0039	0.222	0.407
3	0.0043	0.0042	0.319	0.346
4	0.0051	0.0048	0.249	0.273
5	0.0048	0.0048	0.272	0.446
6	0.0000	0.0046	0.253	0.276
7	0.0000	0.0036	0.280	0.326
8	0.0054	0.0048	0.311	0.239
Avg	0.0031	0.0037	0.280	0.335
Stdev	0.0023	0.0015	0.038	0.067
Max	0.0054	0.0048	0.342	0.446
Min	0.0000	0.0007	0.222	0.239

	Standard deviation (ppb) during evening zero drift tests			
Day	LMA A	LMA B	CSI A	CSI B
0	0.0025	0.0018	0.682	0.301
1	0.0036	0.0034	0.214	0.318
2	0.0005	0.0009	0.301	0.443
3	0.0029	0.0019	0.232	0.395
4	0.0035	0.0024	0.320	0.335
5	0.0013	0.0009	0.255	0.317
6	0.0013	0.0014	0.220	0.389
7	0.0023	0.0081	0.243	0.405
8	0.0026	0.0035	0.262	0.321
Avg	0.0023	0.0027	0.303	0.358
Stdev	0.0010	0.0022	0.146	0.050
Max	0.0036	0.0081	0.682	0.443
Min	0.0005	0.0009	0.214	0.301

TABLE 8. PRECISION MEASUREMENTS FOR NITROGEN DIOXIDE ANALYZERS

		Standard Deviation (ppb) from Precision Tests			
Day	Conc	LMA A	LMA B	CSI A	CSI B
0	0%	0.007	0.007	0.293	0.433
1	0%	0.003	0.003	0.132	0.302
2	0%	0.004	0.000	0.199	0.436
3	0%	0.002	0.005	0.169	0.556
4	0%	0.003	0.002	0.219	0.263
5	0%	0.001	0.001	0.238	0.409
6	0%	0.001	0.001	0.197	0.377
7	0%	0.003	0.002	0.396	0.267
8	0%	0.006	0.002	0.144	0.224
Avg		0.003	0.003	0.221	0.363
Stdev		0.002	0.002	0.082	0.107
Max		0.007	0.007	0.396	0.556
Min		0.001	0.000	0.132	0.224
Day	Conc	LMA A	LMA B	CSI A	CSI B
0	20%	0.048	0.054	0.474	0.189
1	20%	0.097	0.108	0.539	0.811
2	20%	0.062	0.066	0.293	0.408
3	20%	0.053	0.065	0.290	0.556
4	20%	0.026	0.016	0.375	0.295
5	20%	0.030	0.026	0.225	0.490
6	20%	0.016	0.044	0.212	0.223
7	20%	0.014	0.040	0.131	0.396
8	20%	0.012	0.031	0.161	0.303
Avg		0.040	0.050	0.300	0.408
Stdev		0.028	0.028	0.139	0.193
Max		0.097	0.108	0.539	0.811
Min		0.012	0.016	0.131	0.189

(Continued)

TABLE 8. PRECISION MEASUREMENTS FOR NITROGEN DIOXIDE ANALYZERS (Cont'd)

		Standard Deviation (ppb) from Precision Tests			
Day	Conc	LMA A	LMA B	CSI A	CSI B
0	50%	0.081	0.111	0.371	0.401
1	50%	0.140	0.046	0.423	0.267
2	50%	0.076	0.059	0.335	0.536
3	50%	0.026	0.064	0.407	0.372
4	50%	0.070	0.147	0.240	0.245
5	50%	0.054	0.051	0.378	0.269
6	50%	0.030	0.052	0.133	0.259
7	50%	0.047	0.125	0.143	0.598
8	50%	0.058	0.047	0.268	0.328
Avg		0.065	0.078	0.300	0.364
Stdev		0.034	0.039	0.110	0.128
Max		0.140	0.147	0.423	0.598
Min		0.026	0.046	0.133	0.245
Day	Conc	LMA A	LMA B	CSI A	CSI B
0	80%	0.131	0.221	0.391	0.429
1	80%	0.079	0.120	0.322	0.324
2	80%	0.107	0.089	0.263	0.173
3	80%	0.091	0.083	0.274	0.421
4	80%	0.062	0.135	0.276	0.404
5	80%	0.145	0.122	0.356	0.471
6	80%	0.094	0.058	0.203	0.622
7	80%	0.113	0.464	0.261	0.506
8	80%	0.119	0.190	0.327	0.482
Avg		0.105	0.165	0.297	0.426
Stdev		0.026	0.124	0.057	0.125
Max		0.145	0.464	0.391	0.622
Min		0.062	0.058	0.203	0.173

as a function of concentration for the LMA 3 analyzers, but not for the CSI 1600 analyzers. To verify this observation, a statistical analysis was performed on the mean on the nine days' precision values for each analyzer at each concentration. Plots of mean precision versus concentration are shown as Figures 6 and 7. A regression of the average precision values as the dependent variable versus concentration as the independent variable (Table 9) shows a variation of precision with concentration for the LMA 3 analyzers, with coefficients of determination (r^2) of 0.96 and 0.93. No concentration dependence is seen for the CSI 1600 analyzers (r^2 values of 0.47 and 0.26). The effect that variation of precision with concentration for the LMA 3 analyzers has with respect to the calculation of detection and quantitation limits will be discussed in the next subsection.

Detection Limits

As described in the section on test procedures, above, there are two types of detection limits that are evaluated, the limit of detection (LOD) (9) and the lower detection limit (LDL) (2). In addition, the limit of quantitation (LOQ) is evaluated. Implicit in the definitions of all three quantities is the assumption that the precision is uniform over the analyzer's range (i.e. the distribution of measurement errors is homoscedastic) (10). Although this assumption appears reasonable for the CSI 1600 analyzers, a definite increase in precision values (i.e. a decrease in precision) is seen with increasing concentration for the LMA 3 analyzers (Table 9 and Figures 6 and 7). Thus, it was necessary to adjust the estimates of LOD, LDL, and LOQ for the LMA 3 analyzers to account for the concentration-dependent precision values.

The linear regression of precision versus concentration (Table 9) could be used to correct the detection limits for the change in precision seen in the LMA 3 analyzers. However, the use of the regression intercept (see the standard error of the intercepts in Table 9) would introduce a large error into the detection limit calculations. This error would occur because the regression equation is fitted through the centroid of the data which is far from the origin. To avoid this potential error, a regression line was forced through the 0% precision value (Table 10). Inserting the forced regression equation into the definitions of LOD, LDL and LOQ gives the following equations:

$$\text{LOD} = 3\ (\text{precision at } 0\%)/(1-3m),$$

$$\text{LDL} = 2\ (\text{precision at } 0\%)/(1-2m), \text{ and}$$

$$\text{LOQ} = 10\ (\text{precision at } 0\%)/(1-10m),$$

where m is the forced regression slope.

For purposes of comparison, the LMA 3 analyzers' detection limits and LOQ are calculated both assuming that the precision was constant (i.e. the precision value at 0%) and using the above formulas which use the forced regression line. The results of these calculations, as shown in Table 11, lead to two conclusions. First, regardless of the method of calculation, the LMA 3 analyzers have lower detection limits (both LOD and LDL) and a lower LOQ than the CSI 1600 analyzers. Second, the adjustment in LMA 3 detection limits for the concentration-dependent precision values leads to only a very small increase in the detection limit.

TABLE 9. REGRESSION OF MEAN PRECISION VERSUS CONCENTRATION FOR NITROGEN DIOXIDE ANALYZERS

Analyzer	Slope (ppb/ppb)	Intercept (ppb)	Std. Error of Intercept (ppb)	r^2
LMA A	0.0024	0.0087	0.013	0.964
LMA B	0.0038	0.0046	0.030	0.925
CSI A	0.0016	0.251	0.046	0.470
CSI B	0.0009	0.373	0.044	0.258

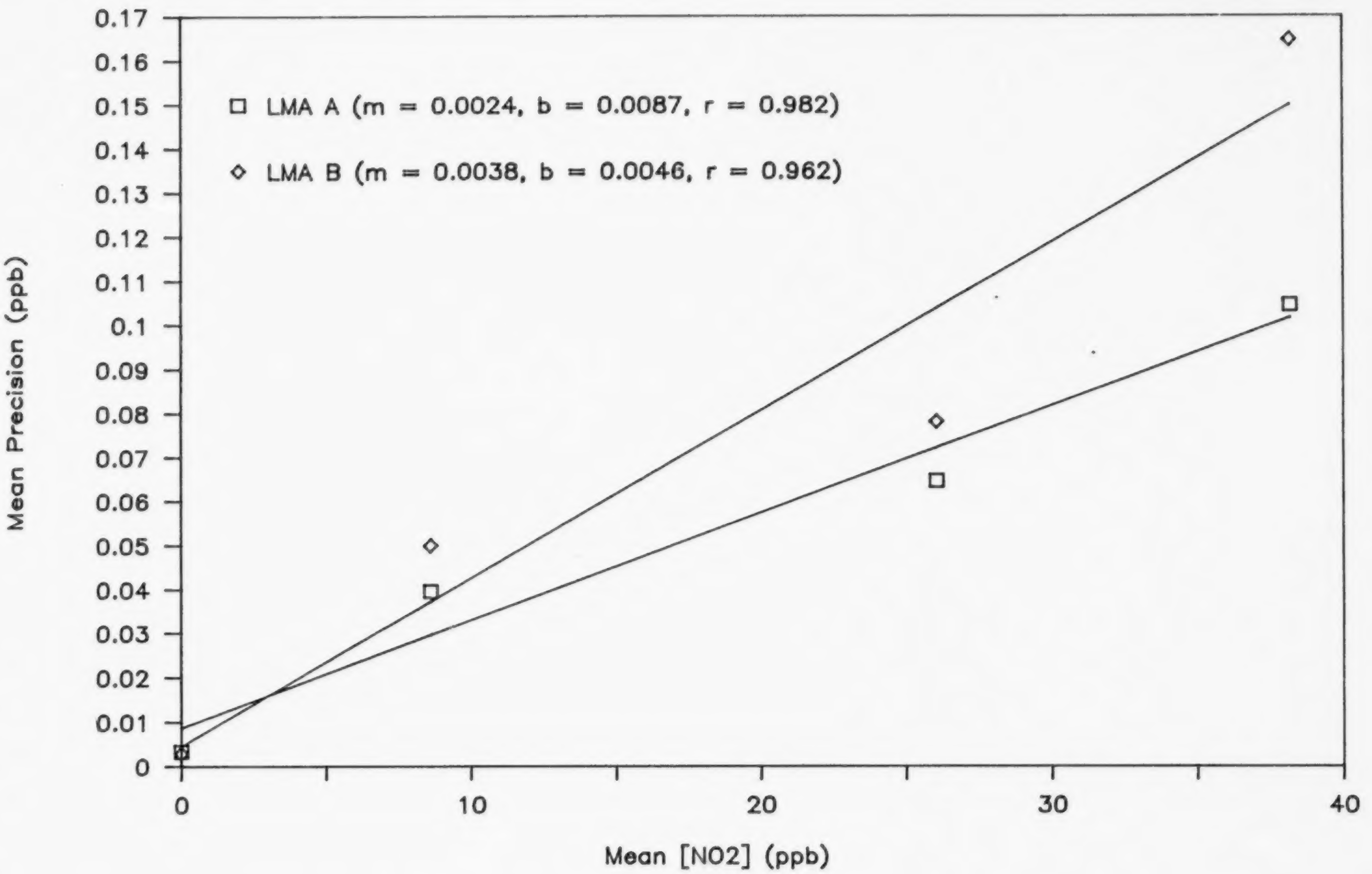

Figure 6. Mean precision versus concentration for LMA 3 NO_2 analyzers

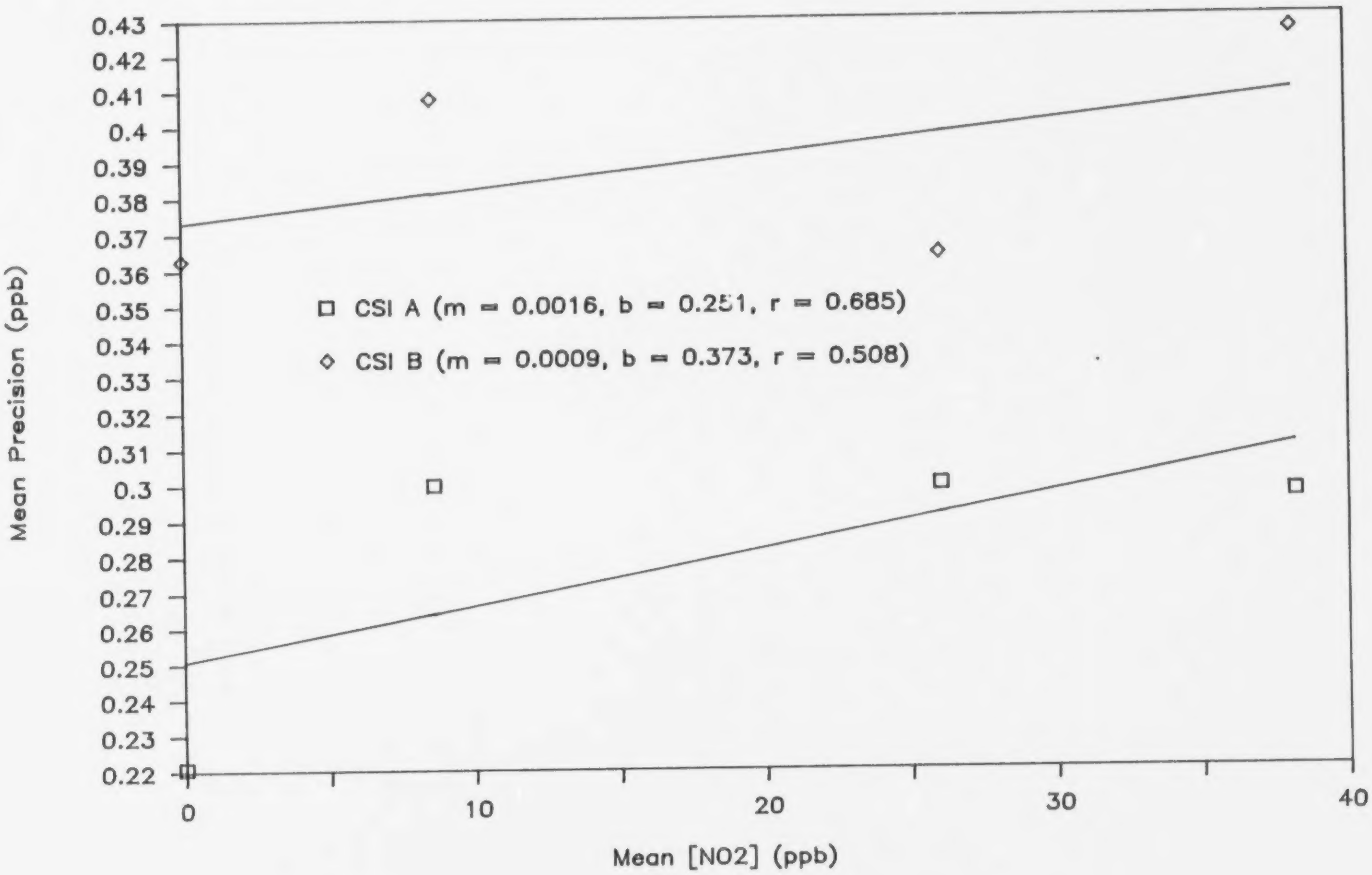

Figure 7. Mean precision versus concentration for CSI 1600 NO_2 analyzers.

TABLE 10. REGRESSION OF MEAN PRECISION VERSUS CONCENTRATION FOR SCINTREX LMA 3 NITROGEN DIOXIDE ANALYZERS, (FORCED THROUGH ZERO-PERCENT PRECISION VALUE)

Analyzer	Slope (ppb/ppb)
LMA A	0.0026
LMA B	0.0013

TABLE 11. DETECTION LIMITS FOR NITROGEN DIOXIDE ANALYZERS

Performance Parameter	Units	LMA A	LMA B	CSI A	CSI B
Limit of Detection [a]	ppb	0.009	0.009	0.663	1.089
Limit of Detection [b]	ppb	0.010	0.009	NA	NA
Limit of Quantitation [c]	ppb	0.030	0.030	2.210	3.630
Limit of Quantitation [d]	ppb	0.034	0.030	NA	NA
Lower Detection Limit [e]	ppb	0.005	0.006	0.560	0.670
Lower Detection Limit [f]	ppb	0.006	0.006	NA	NA

[a] Limit of Detection = 3 (Mean precision at 0%)
[b] Limit of Detection = 3 (Mean precision at 0%)/(1-3m)
[c] Limit of Quantification = 10 (Mean precision at 0%)
[d] Limit of Quantification = 10 (Mean precision at 0%)/(1-10m)
[e] Lower Detection Limit = 2 (Mean noise at 0%)
[f] Lower Detection Limit = 2 (Mean noise at 0%)/(1-2m)

It should also be noted that the estimates of the detection limits were generally consistent within each analyzer model.

Zero, Span and Span Factor Drifts

The zero drifts, span drifts and span factor drifts for the NO_2 analyzers are evaluated according to two different methods. These drifts were measured during a nine-day test cycle in which the environmental chamber temperature and the line voltage were varied. Drift may have occurred independently of the variations or may have been dependent on the variations. In this subsection, the drifts are evaluated as if they are independent of the variations. The average daily drifts are calculated from the daily drifts and are used as the evaluation parameters. If the value of an average daily drift is different from zero, some secular trend in the drift would have occurred. In the next subsection, temperature and voltage matrices are used to evaluate the effect of temperature and voltage on the drifts.

The zero drifts, as shown in Table 12, are presented in units of ppb. They are obtained from the morning and evening average zero noise measurements. They are calculated by multiplying the voltage shift from one day to the next by the next day's span factor (in units of ppb/volt). In general, the daily zero drifts are small and are consistent between the two analyzers of each analyzer model.

The average daily zero drifts for both types of instruments were similar. It should be noted that, although the average zero drifts are near zero, individual daily drifts were much larger, as reflected in the larger standard deviation. This observation suggests that there are no secular trends in the zero values. Maximum daily drifts for the CSI 1600 analyzers exceed those of the LMA 3 analyzers. Overnight drifts for both analyzers, as shown in Table 13, are similar to the daily drifts.

Daily span drifts are calculated from the mean values of the daily 20-, 50- and 80-percent precision measurements. They are presented in units of percent. They are calculated from the relative shift of the mean precision value from one day to the next and are corrected for the slight day-to-day variations in the calibration concentrations. In general, the daily span drifts are consistent between the two analyzers of each analyzer model. The overall parameter that is used to evaluate any secular trends in the analyzers' spans is the average daily span drift across the nine-day test cycle. Average span drifts (Table 14) of both types of instruments are similar. Although the average drift is near zero, individual daily drifts were much larger, as reflected in the increased standard deviation. This observation suggests that there are no secular trends in the span values. The span drifts in Table 14 are not corrected for the day-to-day variations in the zero levels.

As indicated in Table 14, the average daily span drifts at the 20-percent level tend to be larger (in relative terms) than are those at the 50- and 80-percent levels. This effect is likely to be due to the small changes in each analyzer's zero levels over the course of the nine-day test cycle or to the uncertainty in determining the NO_2 calibration concentrations via gas-phase titration.

TABLE 12. DAILY ZERO DRIFTS FOR NITROGEN DIOXIDE ANALYZERS ACROSS TEST DAYS

		Daily morning zero drift (ppb)[a]			
Day	Conc.	LMA A	LMA B	CSI A	CSI B
0	0%	NA	NA	NA	NA
1	0%	0.02	0.04	-0.19	0.05
2	0%	-0.00	-0.00	0.19	-0.05
3	0%	-0.03	-0.06	-0.00	0.19
4	0%	-0.01	-0.03	-0.08	-0.23
5	0%	0.02	0.06	0.02	0.21
6	0%	0.01	0.02	-0.07	-0.16
7	0%	-0.03	-0.06	0.03	0.09
8	0%	0.00	0.00	0.05	0.18
Avg		-0.00	-0.00	-0.01	0.04
Stdev		0.02	0.05	0.11	0.17
Max		0.02	0.06	0.19	0.21
Min		-0.03	-0.06	-0.19	-0.23

		Daily evening zero drift (ppb)[a]			
Day	Conc.	LMA A	LMA B	CSI A	CSI B
0	0%	NA	NA	NA	NA
1	0%	-0.00	0.01	-0.06	-0.10
2	0%	0.02	0.01	-0.20	0.06
3	0%	-0.04	-0.09	0.20	-0.01
4	0%	0.00	0.01	-0.06	0.06
5	0%	0.03	0.07	-0.07	-0.02
6	0%	0.01	0.01	0.10	0.03
7	0%	-0.02	-0.06	0.14	0.19
8	0%	0.01	0.03	-0.06	-0.02
Avg		-0.00	-0.00	-0.00	0.02
Stdev		0.02	0.05	0.13	0.08
Max		0.03	0.07	0.20	0.19
Min		-0.04	-0.09	-0.20	-0.10

[a] Day(n)zero drift = (day(n)span factor) (day(n)zero - day(n-1)zero)

TABLE 13. OVERNIGHT ZERO DRIFTS FOR NITROGEN DIOXIDE ANALYZERS BETWEEN TEST DAYS

		Overnight Zero Drift (ppb)[a]			
Day	Conc.	LMA A	LMA B	CSI A	CSI B
0	0%	NA	NA	NA	NA
1	0%	0.00	0.01	-0.25	-0.07
2	0%	0.00	0.00	-0.00	-0.02
3	0%	-0.04	-0.07	0.20	0.11
4	0%	-0.01	-0.02	-0.08	-0.11
5	0%	0.01	0.04	0.00	0.05
6	0%	-0.00	-0.00	-0.00	-0.09
7	0%	-0.04	-0.07	-0.08	-0.04
8	0%	-0.01	-0.01	-0.17	-0.04
Avg		-0.01	-0.01	-0.05	-0.03
Stdev		0.02	0.04	0.13	0.07
Max		0.01	0.04	0.20	0.11
Min		-0.04	-0.07	-0.25	-0.11

[a] Overnight zero drift = (day (n) span factor) (overnight voltage shift)

TABLE 14. DAILY SPAN DRIFTS FOR NITROGEN DIOXIDE ANALYZERS

		Daily Span Drift [a]			
Day	Conc.	LMA A	LMA B	CSI A	CSI B
0	20%	NA	NA	NA	NA
1	20%	-1.8%	4.3%	-1.5%	-0.5%
2	20%	14.3%	11.4%	6.1%	5.3%
3	20%	-2.5%	-4.8%	4.6%	1.8%
4	20%	-13.8%	-20.4%	-1.2%	2.6%
5	20%	9.9%	8.3%	-6.7%	0.0%
6	20%	-5.1%	-1.3%	3.1%	-2.6%
7	20%	-2.5%	-8.7%	1.3%	5.5%
8	20%	-9.3%	-15.6%	-3.3%	-11.5%
Avg		-1.3%	-3.3%	0.3%	0.1%
Stdev		9.3%	11.3%	4.3%	5.4%
Max		14.3%	11.4%	6.1%	5.5%
Min		-13.8%	-20.4%	-6.7%	-11.5%

Day	Conc.	LMA A	LMA B	CSI A	CSI B
0	50%	NA	NA	NA	NA
1	50%	1.8%	3.9%	2.8%	0.3%
2	50%	9.5%	8.0%	3.0%	2.6%
3	50%	0.9%	1.8%	3.7%	3.1%
4	50%	-10.1%	-19.2%	-5.4%	-0.5%
5	50%	8.5%	9.0%	4.0%	0.9%
6	50%	-4.6%	-2.5%	-3.7%	-2.5%
7	50%	0.7%	-4.0%	3.0%	4.6%
8	50%	-3.4%	-7.1%	-2.7%	-3.4%
Avg		0.4%	-1.2%	0.6%	0.6%
Stdev		6.5%	9.2%	3.8%	2.8%
Max		9.5%	9.0%	4.0%	4.6%
Min		-10.1%	-19.2%	-5.4%	-3.4%

[a] Daily span drift = $100 \left[\frac{\text{day(n) span} - \text{day(n-1) span}}{\text{day (n-1) span}} \right]$

The daily span drifts are corrected for changes in the calibration concentrations.

(Continued)

TABLE 14. DAILY SPAN DRIFTS FOR NITROGEN DIOXIDE ANALYZERS (Cont'd)

		Daily Span Drift[a]			
Day	Conc.	LMA A	LMA B	CSI A	CSI B
0	80%	NA	NA	NA	NA
1	80%	2.6%	3.5%	0.7%	-1.9%
2	80%	8.3%	7.7%	3.1%	4.0%
3	80%	-1.4%	0.5%	2.3%	2.2%
4	80%	-5.8%	-15.4%	-3.7%	-1.4%
5	80%	6.8%	8.2%	3.0%	1.2%
6	80%	-3.3%	-3.4%	-1.6%	-1.1%
7	80%	0.6%	2.1%	2.1%	3.5%
8	80%	-2.0%	-7.3%	-2.0%	-3.8%
Avg		0.7%	-0.5%	0.5%	0.3%
Stdev		4.9%	8.0%	2.6%	2.8%
Max		8.3%	8.2%	3.1%	4.0%
Min		-5.8%	-15.4%	-3.7%	-3.8%

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[a] Daily span drift = $100\left[\frac{\text{day(n) span} - \text{day(n-1) span}}{\text{day(n-1) span}}\right]$

The daily span drifts are corrected for changes in calibration concentrations.

To avoid complications associated with zero drift and to obtain a single parameter to assess the daily span drift, the span data are converted into the daily span factors presented in Table 15. The daily span factors are the slopes of the least-squares regression lines that are calculated from the mean analyzer readings at zero-, 20-, 50-, and 80-percent of full-scale range that were obtained during the daily precision tests. The mean precision values fall very nearly onto a straight line. The coefficients of determination (r^2) for the regressions range from 0.9997 to 1.0000. The daily span factor drifts are calculated from the relative shift of the span factors from one day to the next. In general, the span factor drifts are consistent between the two analyzers of each analyzer model.

The overall parameter that is used to evaluate any secular trends in the span factors is the average span factor drift across the nine-day test cycle. These values range from 0.0 to -1.0 %/day for the NO_2 analyzers. However, the standard deviations of the span factor drifts range from 2.6 to 7.7 %/day. This observation suggests that there are no secular trends in the NO_2 analyzers' span factors. It is likely that the day-to-day variations in the span factors are due to uncertainty in determining the NO_2 calibration concentrations via gas-phase titration.

In summary, there is no evidence of secular trends in the zero and span values for the LMA 3 and CSI 1600 NO_2 analyzers.

Temperature and Voltage Effects on Drift

The zero values and span factors were arranged by temperature and voltage in Tables 16 and 17, respectively. With the daily zero values and daily span factors presented in matrix form, any dependence of these data on temperature or voltage should be apparent. The easiest way to evaluate whether temperature- or voltage-dependent drifts exist is to perform a simple linear regression involving only a single dependent variable (e.g. the zero values) and a single independent variable (e.g. the temperatures). This approach is used to evaluate the data in Tables 16 and 17. A more sophisticated approach would be to perform multiple linear regression involving one dependent variable and three independent variables (i.e. temperature, voltage, and date).

The effect of any secular trends in the drift data is reduced because the measurements at each set of temperatures and voltages are repeated twice. Nevertheless, it is still possible for a secular trend to affect the regression estimates.

Simple linear regression of the LMA 3 analyzers' zero values suggest that these zero values are slightly dependent on temperature, but not on voltage. The results are consistent between the two LMA 3 analyzers and between the morning and evening measurements. The regression of the zero values against the temperatures yielded slopes of approximately -0.003 ppb/°C for LMA(A) and approximately -0.006 ppb/°C for LMA(B). The r^2 for these regressions ranged from 0.74 to 0.85. These values are in good agreement with the value of -0.009 ppb/°C obtained by Bubacz and Pleil (3). The regression of the zero values against the voltages yielded r^2 which ranged from 0.00 to 0.08.

TABLE 15. SPAN FACTORS AND DAILY SPAN FACTOR DRIFTS FOR NITROGEN DIOXIDE ANALYZERS

	Span factors (ppb/V)[a]				Daily drift of span factors[b]			
Day	LMA A	LMA B	CSI A	CSI B	LMA A	LMA B	CSI A	CSI
0	9.687	9.582	55.297	52.666	NA	NA	NA	NA
1	9.420	9.255	54.404	53.465	-2.8%	-3.5%	-1.6%	1.5%
2	8.663	8.557	52.834	51.595	-8.7%	-8.2%	-3.0%	-3.6%
3	8.716	8.434	51.686	50.402	0.6%	-1.5%	-2.2%	-2.4%
4	9.274	9.799	53.932	51.171	6.0%	13.9%	4.2%	1.5%
5	8.615	8.991	51.614	50.580	-7.6%	-9.0%	-4.5%	-1.2%
6	8.948	9.316	53.019	51.219	3.7%	3.5%	2.6%	1.2%
7	8.858	9.146	51.835	49.512	-1.0%	-1.9%	-2.3%	-3.4%
8	9.008	9.748	52.853	51.059	1.7%	6.2%	1.9%	3.0%
Avg	9.021	9.203	53.053	51.297	-1.0%	-0.0%	-0.6%	-0.4%
Stdev	0.368	0.483	1.282	1.186	5.2%	7.7%	3.1%	2.6%
Max	9.687	9.799	55.297	53.465	6.0%	13.9%	4.2%	3.0%
Min	8.615	8.434	51.614	49.512	-8.7%	-9.0%	-4.5%	-3.6%

[a] Determined from the slope of the linear regression of calibration data at zero, 20, 50 and 80 percent full scale.

[b] Day (n) drift = 100 $\left[\frac{\text{Day(n) span factor - day(n - 1) span factor}}{\text{day (n-1) span factor}}\right]$

TABLE 16. TEMPERATURE AND VOLTAGE MATRICES FOR NITROGEN DIOXIDE ANALYZER ZERO VALUES

A) Morning zero values for LMA A (volts)

Temp deg C	Line Voltage 105 V AC	115 V AC	125 V AC
20	Day 2 -0.258 Day 6 -0.262		Day 1 -0.255 Day 5 -0.276
25		Day 0 -0.273	
30	Day 4 -0.297 Day 8 -0.288		Day 3 -0.283 Day 7 -0.291

B) Morning zero values for LMA B (volts)

Temp deg C	Line Voltage 105 V AC	115 V AC	125 V AC
20	Day 2 0.118 Day 6 0.113		Day 1 0.123 Day 5 0.091
25		Day 0 0.080	
30	Day 4 0.026 Day 8 0.059		Day 3 0.056 Day 7 0.057

(Continued)

TABLE 16. TEMPERATURE AND VOLTAGE MATRICES FOR NITROGEN DIOXIDE ANALYZER ZERO VALUES (Cont'd)

C) Morning zero values for CSI A (volts)

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 0.037 Day 6 -0.095		Day 1 -0.155 Day 5 -0.022
25		Day 0 0.034	
30	Day 4 -0.042 Day 8 -0.021		Day 3 0.037 Day 7 -0.068

D) Morning zero values for CSI B (volts)

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 0.047 Day 6 0.056		Day 1 0.096 Day 5 0.221
25		Day 0 0.043	
30	Day 4 0.006 Day 8 0.324		Day 3 0.235 Day 7 0.144

(Continued)

TABLE 16. TEMPERATURE AND VOLTAGE MATRICES FOR NITROGEN DIOXIDE ANALYZER ZERO VALUES (Cont'd)

E) Evening zero values for LMA A (volts)

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 -0.246 Day 6 -0.252		Day 1 -0.261 Day 5 -0.257
25		Day 0 -0.257	
30	Day 4 -0.283 Day 8 -0.267		Day 3 -0.284 Day 7 -0.276

F) Evening zero values for LMA B (volts)

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 0.131 Day 6 0.126		Day 1 0.117 Day 5 0.117
25		Day 0 0.108	
30	Day 4 0.048 Day 8 0.099		Day 3 0.042 Day 7 0.069

(Continued)

TABLE 16. TEMPERATURE AND VOLTAGE MATRICES FOR NITROGEN DIOXIDE ANALYZER ZERO VALUES (Cont'd)

G) Evening zero values for CSI A (volts)

Temp deg C	Line Voltage 105 V AC	115 V AC	125 V AC
20	Day 2 -0.164 Day 6 0.010		Day 1 0.041 Day 5 -0.093
25		Day 0 0.098	
30	Day 4 -0.022 Day 8 0.093		Day 3 0.038 Day 7 0.148

H) Evening zero values for CSI B (volts)

Temp deg C	Line Voltage 105 V AC	115 V AC	125 V AC
20	Day 2 0.128 Day 6 0.179		Day 1 0.066 Day 5 0.148
25		Day 0 0.165	
30	Day 4 0.171 Day 8 0.347		Day 3 0.115 Day 7 0.366

TABLE 17. TEMPERATURE AND VOLTAGE MATRICES FOR NITROGEN DIOXIDE SPAN FACTORS

A) Span factors for LMA A (ppb/volt)

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 8.663 Day 6 8.948		Day 1 9.420 Day 5 8.615
25		Day 0 9.687	
30	Day 4 9.274 Day 8 9.008		Day 3 8.716 Day 7 8.858

B) Span factors for LMA B (ppb/volt)

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 8.557 Day 6 9.316		Day 1 9.255 Day 5 8.991
25		Day 0 9.582	
30	Day 4 9.799 Day 8 9.748		Day 3 8.434 Day 7 9.146

(Continued)

TABLE 17. TEMPERATURE AND VOLTAGE MATRICES FOR NITROGEN DIOXIDE SPAN FACTORS (Cont'd)

C) Span factors for CSI A (ppb/volt)

Temp deg C	Line Voltage 105 V AC	115 V AC	125 V AC
20	Day 2 52.834 Day 6 53.019		Day 1 54.404 Day 5 51.614
25		Day 0 55.297	
30	Day 4 53.932 Day 8 52.853		Day 3 51.686 Day 7 51.835

D) Span factors for CSI B (ppb/volt)

Temp deg C	Line Voltage 105 V AC	115 V AC	125 V AC
20	Day 2 51.595 Day 6 51.219		Day 1 53.465 Day 5 50.580
25		Day 0 52.666	
30	Day 4 51.171 Day 8 51.059		Day 3 50.402 Day 7 49.512

Simple linear regression of the CSI 1600 analyzers' zero values suggest that these zero values are not dependent on either temperature or voltage. The regression of the zero values against the temperatures yielded r^2 which ranged from 0.07 to 0.35. The regression of the zero values against the voltages yielded r^2 which ranged from 0.03 to 0.09.

Simple linear regression of the LMA 3 analyzers' span factors suggest that these span factors are not dependent on either temperature or voltage. The regression of the span factors against the temperatures yielded r^2 of 0.01 and 0.07. The regression of the span factors against the voltages yielded r^2 of 0.01 and 0.17.

Simple linear regression of the CSI 1600 analyzers' span factors suggest that these span factors are not dependent on either temperature or voltage. The regression of the span factors against the temperatures yielded r^2 of 0.02 and 0.24. The regression of the span factors against the voltages yielded r^2 of 0.01 and 0.25.

In summary, the LMA 3 NO_2 analyzers exhibit a slight temperature-dependent zero drift. The CSI 1600 analyzers' zero values showed no temperature or voltage dependence. The span factors for both the LMA and the CSI NO_2 analyzers were free from dependence on temperature or voltage.

The span factor drift results for the LMA 3 NO_2 analyzers are considerably different from the results of Bubacz and Pliel (3). They tested an earlier version of this instrument which was not temperature-controlled or temperature compensated. At a constant NO_2 concentration of 190 ppb, they found a significant span drift as a function of temperature (20 to 40°C). The change in response equaled 4 ppb/°C. Subsequently, Bubacz et al. reported a field evaluation of two LMA 3 NO_2 analyzers employing different temperature-dependence correction methods (28). One analyzer used temperature-sensing electronics to compensate the output signal. The other analyzer used feedback-controlled heating to maintain the analyzer's reaction. However, they did not perform any explicit temperature dependence tests. This research demonstrates that the temperature-dependent span factor drift problem has been eliminated.

Response Times

The LMA 3 NO_2 analyzers had significantly shorter rise and fall times than had the CSI 1600 NO_2 analyzers (see Tables 18 and 19). Interestingly, the LMA 3 analyzers had much shorter fall times (Table 15) than rise times. Although the reason for the difference between these times is unknown, this difference may reflect the time required to condition the walls of the sample manifold with NO_2 or it may reflect an actual performance characteristic of the LMA 3 NO_2 analyzers.

As was noted in the section on test procedures, the rise time is the time between the initial response to a step concentration change and a reading equal to 95 percent of the final value. Although the LMA 3 NO_2 analyzers had short rise times, they had long stabilization times which were only seen during the initial 80-percent precision test after sampling zero air overnight. The analyzers quickly reached approximately 95 percent of their final, stable readings, but then only slowly reached their final,

TABLE 18. RISE TIMES FOR NITROGEN DIOXIDE ANALYZERS

		Rise Time in minutes			
Day	Test	LMA 3		CSI 1600	
		A	B	A	B
0	1	1.9	2.0	4.4	4.2
0	2	2.2	2.3	4.9	4.0
0	3	2.1	2.3	4.2	4.1
1	1	1.8	1.6	4.8	5.4
1	2	1.5	1.8	4.9	4.0
1	3	1.1	1.6	5.4	4.0
2	1	--[a]	--[a]	4.3	4.6
2	2	1.8	1.9	4.4	4.2
2	3	1.8	1.8	4.0	4.2
3	1	--[a]	--[a]	5.3	4.9
3	2	1.8	1.8	4.7	3.9
3	3	1.5	1.8	5.8	4.8
4	1	1.8	2.3	5.1	4.1
4	2	1.8	2.1	5.0	4.3
4	3	1.9	2.3	5.2	4.7
5	1	1.7	1.8	4.4	4.7
5	2	1.9	1.8	4.3	4.2
5	3	2.2	1.7	4.3	4.4
6	1	1.7	2.0	4.0	4.2
6	2	2.1	1.8	4.9	4.2
6	3	1.5	1.5	4.8	3.9
7	1	2.1	1.9	5.2	4.4
7	2	1.8	1.9	5.7	4.1
7	3	1.9	2.2	5.0	4.1
8	1	2.0	2.1	5.3	4.1
8	2	2.0	2.1	5.8	4.3
8	3	1.9	2.1	6.2	4.5
Avg		1.8	1.9	4.9	4.3
Stdev		0.2	0.2	0.6	0.3
Max		2.2	2.3	6.2	5.4
Min		1.1	1.5	4.0	3.9

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[a] Data not available because the strip chart recorder's chart speed was too slow to obtain adequate time resolution.

TABLE 19. FALL TIMES FOR NITROGEN DIOXIDE ANALYZERS

		Fall Time in minutes			
		LMA 3		CSI 1600	
Day	Test	A	B	A	B
0	1	0.2	0.2	4.4	3.2
0	2	0.3	0.2	4.2	3.2
0	3	0.1	0.2	4.6	3.1
1	1	0.3	0.3	3.9	3.7
1	2	0.2	0.1	4.0	3.7
1	3	0.2	0.2	4.3	5.4
2	1	--[a]	--[a]	--[a]	3.5
2	2	0.2	0.1	3.9	3.4
2	3	0.3	0.4	4.0	3.7
3	1	--[a]	--[a]	--[a]	3.3
3	2	0.2	0.2	4.6	3.2
3	3	0.3	0.3	4.9	3.6
4	1	0.2	0.5	4.1	3.8
4	2	0.1	0.2	3.9	3.8
4	3	0.1	0.4	4.7	3.7
5	1	0.2	0.3	3.8	3.4
5	2	0.2	0.2	3.7	4.2
5	3	0.2	0.5	3.3	3.6
6	1	--[a]	--[a]	--[a]	--[a]
6	2	0.1	0.2	3.9	3.7
6	3	0.2	0.6	3.8	3.9
7	1	0.2	0.4	5.2	5.7
7	2	0.1	0.3	5.2	4.1
7	3	0.1	0.3	3.6	4.1
8	1	0.3	0.2	4.6	3.8
8	2	0.1	0.2	3.9	4.0
8	3	0.1	0.2	4.9	3.5
Avg		0.2	0.3	4.2	3.8
Stdev		0.1	0.1	0.5	0.6
Max		0.3	0.6	5.2	5.7
Min		0.1	0.1	3.3	3.1

[a] Data not available because the strip chart recorder's chart speed was too slow to obtain adequate time resolution.

stable readings. Approximately 3 hours were needed to obtain the final, stable readings. This phenomenon was not seen during subsequent step concentration changes during each test day. It is hypothesized that the stabilization phenomenon is associated with conditioning the LMA 3 analyzers' ozone traps. Manifold conditioning could not be the cause of the phenomenon because the CSI 1600 analyzers were not affected.

Interferences

The results of the interference tests are presented in Table 20. In general, the interference tests were conducted in the presence of a NO_2 concentration equal to 50 percent (i.e. 25 ppb) of the full scale range. An analyzer is considered to have a measurable response to a given interferent if the difference between the response with and without the interferent exceeded the 95% confidence limits for the analyzers response at 50% concentration. These limits were obtained by multiplying 1.96 times the precision at 50% concentration (Table 8). Each analyzer produced measurable responses to more than one interferent. The results are discussed in separate sections by interferent below.

Oxygen --

Oxygen (O_2) interference was tested by replacing the dilutant zero air ($[O_2]$ approximately 21%) with dilutants of nitrogen and other concentrations of O_2. Two such dilutants were used. First, pure nitrogen ($[O_2]$ = 0%) was used as a dilutant. Although both types of analyzers showed measurable interference, the LMA 3 analyzers' response virtually disappeared. Second, a mixture of 37% O_2 in nitrogen was used as an interferent. No measurable interference was seen in the CSI 1600 analyzers. The relative interference response of the LMA 3 NO_2 analyzers tothe 37% O_2 was approximately 3.2×10^{-8} ppb/ppb, which is approximately a factor of four less than the corresponding response to nitrogen. The reason for this difference in relative interference responses is unknown, but may indicate participation by O_2 in the luminol-based chemiluminescent reaction.

Although the O_2 concentration in ambient air is largely constant and no O_2-dependent effects should be seen in ambient air measurements, the results of these tests indicate possible problems for calibration of the LMA 3 analyzers unless the O_2 concentration of the calibration mixtures is controlled. The CSI 1600 analyzers are sufficiently insensitive to O_2 that use of zero air rather than nitrogen for calibration mixtures should be adequate. However an oxygen concentration variation of approximately +/- 2 percent (absolute) may occur in compressed synthetic zero air (ref. 29). Such a concentration variation would lead to a analyzer response variation of approximately +/- 0.6 ppb at 26.5 ppb or +/- 2 percent of the total response in the LMA 3 analyzers. This response variation is outside the 95-percent confidence limits of the LMA 3 analyzers at this concentration. Whether this variation in response due to O_2 interference would be acceptable would depend on the individual study.

Carbon Dioxide --

No carbon dioxide (CO_2) interference was seen on the CSI 1600 analyzers. The LMA 3 analyzers saw measurable interference. The relative interferent effect was similar at two different CO_2 concentrations. Although the atmospheric CO_2 concentration may not vary appreciably in the

Table 20. Interference Test Results for Nitrogen Dioxide Analyzers

Species	[Species] (ppb)	[NO_2] (ppb)	Change in [NO_2] LMA A (ppb)	Change in [NO_2] LMA B (ppb)	Change in [NO_2] CSI A (ppb)	Change in [NO_2] CSI B (ppb)	Relative Interference Response = change in [NO_2] (ppb) / [interferent] (ppb) LMA A	LMA B	CSI A	CSI B	Notes
O_2	-2.1E+08	26.50	-25.60	-25.80	-1.6	-1.7	1.2E-07	1.2E-07	7.7E-09	8.1E-09	1
O_2	1.6E+08	26.50	4.72	5.50	ND	ND	3.0E-08	3.4E-08	ND	ND	2
CO_2	7.5E+05	25.50	-3.19	-3.99	ND	ND	-4.2E-06	-5.3E-06	ND	ND	3
CO_2	3.7E+05	25.50	-1.31	-1.77	ND	ND	-3.5E-06	-4.6E-06	ND	ND	3
H_2O	1.3E+07	26.40	-1.74	-2.35	-0.72	-0.87	-1.4E-07	-1.8E-07	-5.6E-08	-6.8E-08	4
SO_2	4.3E+02	26.10	0.52	ND	0.61	ND	1.2E-03	ND	1.4E-03	ND	
HCl	2.7E+02	26.10	0.67	0.16	ND	ND	2.5E-03	5.9E-04	ND	ND	
NH_3	3.3E+02	26.10	ND	ND	19.17	59.08	ND	ND	5.8E-02	1.8E-01	5
O_3	4.3E+02	0.00	ND	ND	ND	ND	ND	ND	ND	ND	
PAN	1.4E+01	25.62	9.69	7.80	13.94	14.25	6.9E-01	5.5E-01	NA	NA	6
HNO_3	9.5E+00	0.00	ND	ND	9.75	10.31	ND	ND	1.0E+00	1.1E+00	
HNO_2	4.8E+00	0.00	1.97	2.75	4.79	4.91	4.1E-01	5.7E-01	NA	NA	7
HNO_2	5.3E+00	0.00	1.95	2.85	5.22	5.33	3.7E-01	5.4E-01	NA	NA	7

ND = Change is within 95% confidence limits based on 1.96 times the standard deviation at 50% of full scale concentration.

NA = Not applicable. The CSI 1600 analyzers were used to determine the interferent species concentration.

Key to exponential notation: -2.1 E + 08 is equivalent to $-2.1 \times 10^{+8}$

Notes:

1. N_2 used as dilutant in place of zero air. Change is relative to zero air.
2. O_2 at a concentration of 37% was used as dilutant. Change is relative to zero air.
3. CO_2 concentration is that of spike above the CO_2 present in zero air.
4. The interferent concentration is the difference between 5.0×10^6 ppb (i.e. 16% relative humidity at 25RC) and 1.8×10^7 ppb (i.e. 56% relative humidity at 25RC).
5. Response to NH_3 was seen only after greater than 2 hours. This time may represent conditioning of manifold to NH_3. The interference was measured on the 0 to 100 ppb range.
6. Concentration of PAN (peroxy acetyl nitrate) is based on CSI response, assuming that the CSI NO2 channel measures PAN directly (i.e. 100% response).
7. Nitrous acid (HNO_2) generator was unstable. The output dropped approximately 0.5 to 1.0 ppb during the measurement period. The HNO_2 concentration was calculated assuming that the difference in CSI NO_2 response with and without K_2CO_3 coated filters was due to HNO_2 (with 100% response).

short term, the difference between calibration with synthetic zero air (without CO_2) and sampling with ambient air (approximately 350 ppm CO_2) would give a difference in LMA 3 NO_2 response on the order of 1 to 2 ppb at a NO_2 concentration of 25 ppb (or a 5 to 7% error). For this reason, it is important to calibrate the LMA 3 analyzer with calibration mixtures containing ambient levels of CO_2.

Water --

The dilution air used in the laboratory evaluation (see description of the zero air system in the Test Procedures section, above) generally is very dry with a dew-point of below -10 degrees C. At the suggestion of Scintrex representatives that problems might be experienced with drying of the wick and reaction surface of the LMA 3 analyzers, the dilution air for the laboratory evaluation was humidified by passage through a flask containing water. The dew-point in the sampling manifold was measured to be -2.5 degrees C (i.e., $[H_2O]$ = 5000 ppm) by use of an EG&G model 660 dew-point hydrometer.

The water interference test was performed by comparing the analyzers' responses to airstreams having identical NO_2 concentrations, but differing H_2O concentrations. The dewpoints of the two airstreams were -2.5 and 16 degrees C. The corresponding H_2O concentrations were approximately 5000 and 18,000 ppm, respectively. Measurable water interference was seen on both types of analyzers. For an estimate of the impact that water interference would have on analyzer response, consider a change from 10% relative humidity to 80% relative humidity at 100 degrees Fahrenheit (37 degrees C). This corresponds to a change in the water concentration of 34 Torr or 4.5×10^7 ppbv. This would result in a change for the LMA 3 analyzers of approximately -7 ppb at a concentration of 25 ppb or a 29% error. The CSI analyzers would change by approximately -3 ppb at a concentration of 25 ppb or a 11% error.

As noted in the section on test procedures, the calibration gas mixtures prepared during the field evaluation were not humidified. Based on these water interference test results, one would expect some bias in NO_2 measurements of humidified ambient air because of the use of dry calibration gas mixtures. The magnitude of this bias was not estimated for the NO_2 measurements during the field evaluation. It will vary from day to day as ambient humidity levels vary.

Sulfur Dioxide --

Although measurable levels of SO_2 interference were seen on one of each type of analyzers, the relative interferent response was very low (approximately 1×10^{-3} ppb NO_2 per ppb SO_2). No measurable response was seen on the other analyzer of each type. This is due to the interference being near the 95% confidence interval for the NO_2 precision at this concentration. This level of interference would only pose an interferent problem at SO_2 levels found in heavily polluted areas. At the maximum levels permitted by the National Ambient Air Quality Standards (1) of 30 ppb for an annual arithmetic mean and 140 ppb for a 24 hour average this would give interference levels of 0.03 ppb for the annual mean and 0.14 ppb for the 24 hour level. Both interference levels are below the lower detection limit for the CSI 1600 analyzers.

Hydrogen Chloride --

Although measurable levels of HCl interference were seen on the LMA 3 analyzers, the relative interferent response was very low (approximately 0.5 to 3 x 10^{-3} ppb NO_2 per ppb HCl). Using an ambient level in clean air of approximately 1 ppb (30), one calculates an interference level of 0.5 to 3 ppt. This interference level is below the limit of detection (Table 9), and it is not anticipated that noticeable interference to HCl will be seen in most ambient measurements.

Ammonia --

The LMA 3 analyzers showed no measurable response to ammonia (NH_3). As described above under test procedures, at first the CSI 1600 analyzers also showed no interference to ammonia. This observation would agree with earlier work by Bass and Mitchie (31). However, at longer exposure times, a measurable ammonia response of approximately 0.06 to 0.18 ppb NO_2 response per ppb NH_3 was seen. At the ammonia interferent concentration of 330 ppb, the interference was great enough to require the use of the 0 to 100 ppb full scale range on the CSI 1600 analyzers. With a precision for NO_2 at 0% of approximately 0.3 ppb, this would indicate a detection limit for NH_3 as NO_2 on the order of between 2 to 5 ppb. This is potential problem for use of the CSI 1600 analyzers in ambient monitoring.

Ozone --

No measurable response to ozone (O_3) was seen on either type of instrument. Luminol-based chemiluminescent analyzers had shown O_3 interference in other tests (4, 5). The lack of interference is likely due to the use of ozone traps which were supplied by Scintrex.

Peroxyacetyl Nitrate (PAN) --

In earlier work it was shown that gas phase chemiluminescence NO_2 analyzers have approximately quantitative response to PAN (ref. 23). Due to the difficulties in producing a PAN calibration mixture of known concentration, it was decided to use the CSI 1600 NO_2 channel response to PAN as a measure of the PAN concentration for testing the LMA 3 analyzers. The LMA 3 analyzers saw 69% and 55% (for A and B respectively) of the average CSI response to PAN. The relative responses of the LMA 3 analyzers to PAN are less than the quantitative response observed by Wendel et al. in a similar instrument employing the luminol reaction (4). Sickles et al. reported relative interference responses of between 0.50 and 0.55 for LMA 3 analyzers (18).

Nitric Acid --

The LMA 3 analyzers saw no measurable response to nitric acid (HNO_3), while the CSI 1600 analyzers saw essentially quantitative response to HNO_3.

Nitrous Acid --

The nitrous acid interference test was performed at the end of the field evaluation, rather than during the laboratory evaluation. Nitrous acid (HNO_2) was generated by use of a sublimation generator similar to that used by Braman and de la Cantera (24). Further details are given in the test procedures section, above. The output HNO_2 concentration of this generator is not very stable. Due to the long time required for filter loading and the instability of the generator, verification of the HNO_2

concentration by filter samples was not attempted. It was assumed that the CSI 1600 analyzers had quantitative response to HNO_2. The LMA 3 analyzers' response was thus measured relative to that of the CSI 1600 analyzers. In addition, the generator may produce small amounts of NO, NO_2, and HNO_3. A nylon filter was placed on the generator output to collect any HNO_3 that might be present. The difference between the responses with and without an additional Na_2CO_3 coated filter (which collects HNO_2) was taken as response to HNO_2. The two LMA 3 analyzers saw 37% and 54% of the average CSI 1600 analyzers' response (for LMA A and LMA B respectively). The interference of HNO_2 in the LMA 3 analyzers has not been reported in the literature previously.

LABORATORY EVALUATION OF SULFUR DIOXIDE ANALYZERS

Maintenance and Operational Failures

No maintenance was performed on the TECO 43S SO_2 analyzers during the laboratory evaluation. No failure of either instrument was experienced.

Noise

Noise measurements, at zero concentration, for the Thermo Environmental model 43S analyzers are shown in Table 21. One analyzer (TECO A) consistently had noise levels that were twice those of the other analyzer (TECO B). Nevertheless, the noise levels for both analyzers are small in comparison with the analyzers' full scale range.

Precision

Precision measurements, expressed as the standard deviation of repeated measurements, are given in Table 22. Precision measurements were made at zero, 20, 50, and 80 percent of the analyzers' full scale range. The precision values for one analyzer (TECO A) were consistently larger than those of the other analyzer (TECO B). A qualitative review of the precision values for both analyzers suggests that the precision varied as a function of concentration. A plot of the average precision values over the nine-day test cycle versus concentration is shown as Figure 7. To verify the observation of concentration-dependent precision values, a statistical analysis was performed on the mean of the nine days' precision values for each analyzer at each concentration. A regression of the nine-day average precision values as the dependent variable against concentration as the independent variable (Table 23) shows variation of precision with concentration for the TECO model 43S analyzers, with coefficients of determination (r^2) of 0.96 and 0.98. The effect that variation of precision with concentration has with respect to the calculation of detection and quantitation limits is discussed later.

Detection Limits

As described in the section on NO_2 analyzers, above, there are two types of detection limits that are evaluated, the limit of detection (LOD) (9) and the lower detection limit (LDL) (2). In addition, the limit of quantitation (LOQ) is evaluated. Implicit in the definitions of all three

TABLE 21. NOISE MEASUREMENTS FOR SULFUR DIOXIDE ANALYZERS

Day	Standard Deviation (ppb) During Morning Zero Drift Tests	
	TECO A	TECO B
0	0.0311	0.0148
1	0.0342	0.0114
2	0.0338	0.0173
3	0.0231	0.0186
4	0.0336	0.0178
5	0.0464	0.0196
6	0.0333	0.0130
7	0.0284	0.0130
8	0.0246	0.0163
Avg	0.0321	0.0158
Stdev	0.0068	0.0028
Max	0.0464	0.0196
Min	0.0231	0.0114

Day	Standard Deviation (ppb) During Evening Zero Drift Tests	
	TECO A	TECO B
0	0.0231	0.0138
1	0.0345	0.0103
2	0.0307	0.0177
3	0.0313	0.0159
4	0.0403	0.0207
5	0.0369	0.0122
6	0.0335	0.0116
7	0.0337	0.0183
8	0.0315	0.0183
Avg	0.0328	0.0154
Stdev	0.0047	0.0036
Max	0.0403	0.0207
Min	0.0231	0.0103

TABLE 22. PRECISION MEASUREMENTS FOR SULFUR DIOXIDE ANALYZERS

		Standard Deviation from Precision Tests (ppb)	
Day	Conc	TECO A	TECO B
0	0%	0.0260	0.0153
1	0%	0.0441	0.0101
2	0%	0.0317	0.0169
3	0%	0.0137	0.0220
4	0%	0.0351	0.0186
5	0%	0.0309	0.0089
6	0%	0.0263	0.0158
7	0%	0.0242	0.0224
8	0%	0.0310	0.0165
Avg		0.0292	0.0163
Stdev		0.0083	0.0046
Max		0.0441	0.0224
Min		0.0137	0.0089

Day	Conc	TECO A	TECO B
0	20%	0.0453	0.0250
1	20%	0.0472	0.0132
2	20%	0.0105	0.0244
3	20%	0.0550	0.0105
4	20%	0.0320	0.0185
5	20%	0.0485	0.0148
6	20%	0.0394	0.0153
7	20%	0.0338	0.0100
8	20%	0.0315	0.0228
Avg		0.0381	0.0172
Stdev		0.0132	0.0058
Max		0.0550	0.0250
Min		0.0105	0.0100

(Continued)

TABLE 22. PRECISION MEASUREMENTS FOR SULFUR DIOXIDE ANALYZERS (Cont'd)

		Standard Deviation from Precision Tests (ppb)	
Day	Conc	TECO A	TECO B
0	50%	0.0706	0.0255
1	50%	0.0505	0.0180
2	50%	0.0418	0.0450
3	50%	0.0423	0.0163
4	50%	0.0440	0.0339
5	50%	0.0298	0.0280
6	50%	0.0698	0.0195
7	50%	0.0327	0.0349
8	50%	0.0333	0.0253
Avg		0.0461	0.0274
Stdev		0.0151	0.0093
Max		0.0706	0.0450
Min		0.0298	0.0163
Day	Conc	TECO A	TECO B
0	80%	0.0392	0.0279
1	80%	0.0613	0.0374
2	80%	0.0849	0.0289
3	80%	0.0329	0.0361
4	80%	0.0827	0.0408
5	80%	0.0290	0.0375
6	80%	0.0409	0.0236
7	80%	0.0347	0.0431
8	80%	0.0673	0.0426
Avg		0.0525	0.0353
Stdev		0.0219	0.0070
Max		0.0849	0.0431
Min		0.0290	0.0236

lyzer range (i.e., the distribution of measurement errors is homoscedastic) (4). Since the precision varies with concentration (Table 23, Figure 8), it was necessary to adjust the estimates of LOD, LDL, and LOQ for the TECO 43S analyzers to account for the concentration - dependent precision values.

The linear regression of precision versus concentration (Table 23) could be used to compensate for the change in precision seen by the analyzers. However, the use of the regression intercept (see the standard error of intercept in Table 23), rather than the mean zero-percent precision value, would introduce a large error into the detection limit calculations. This error is due to the fact that the regression equation is fitted through the centroid of the data, which is far from the origin. To reduce this error, a regression line was forced through the mean zero-percent precision value (Table 24). Inserting the forced regression equation into the definitions of LOD, LDL and LOQ gives the following equations:

$$\text{LOD} = 3(\text{precision at } 0\%)/(1-3m),$$

$$\text{LDL} = 2(\text{precision at } 0\%)/(1-2m), \text{ and}$$

$$\text{LOQ} = 10(\text{precision at } 0\%)/(1-10m)$$

where m is the forced regression slope.

Detection limits for the TECO 43S analyzers are presented in Table 25. For purposes of comparison, the detection limits and LOQ are calculated both assuming that the precision was constant (i.e. the mean noise or precision value at zero percent) and using the above formulas which use the forced regression line (Table 24). The adjustment in detection limits for the concentration-dependent precision leads to only a very small change in the detection limits.

The detection limits for one analyzer (TECO A) are consistently less than those for the other analyzer (TECO B). Nevertheless, the detection limits for both analyzers are small in comparison with the analyzers' full scale range.

Zero Span and Span Factor Drifts

The zero drifts, span drifts, and span factor drifts for the SO_2 analyzers are evaluated according to two different methods. These drifts were measured during a nine-day test cycle in which the environmental chamber temperature and the line voltage were varied. Drift may have occurred independently of the variations or may have been dependent on the variations. First, the drifts are evaluated in this subsection as if they are independent of the variations. Nine-day average drifts are calculated and are used as the evaluation parameters. If the value of an average drift is different from zero, some secular trend exists in the drift data. The second method that is used to evaluate drift is through the use of a temperature and voltage matrix. This method assumes that no secular trend exists and all change in the drift is due to temperature and voltage variations. It is discussed in the next subsection.

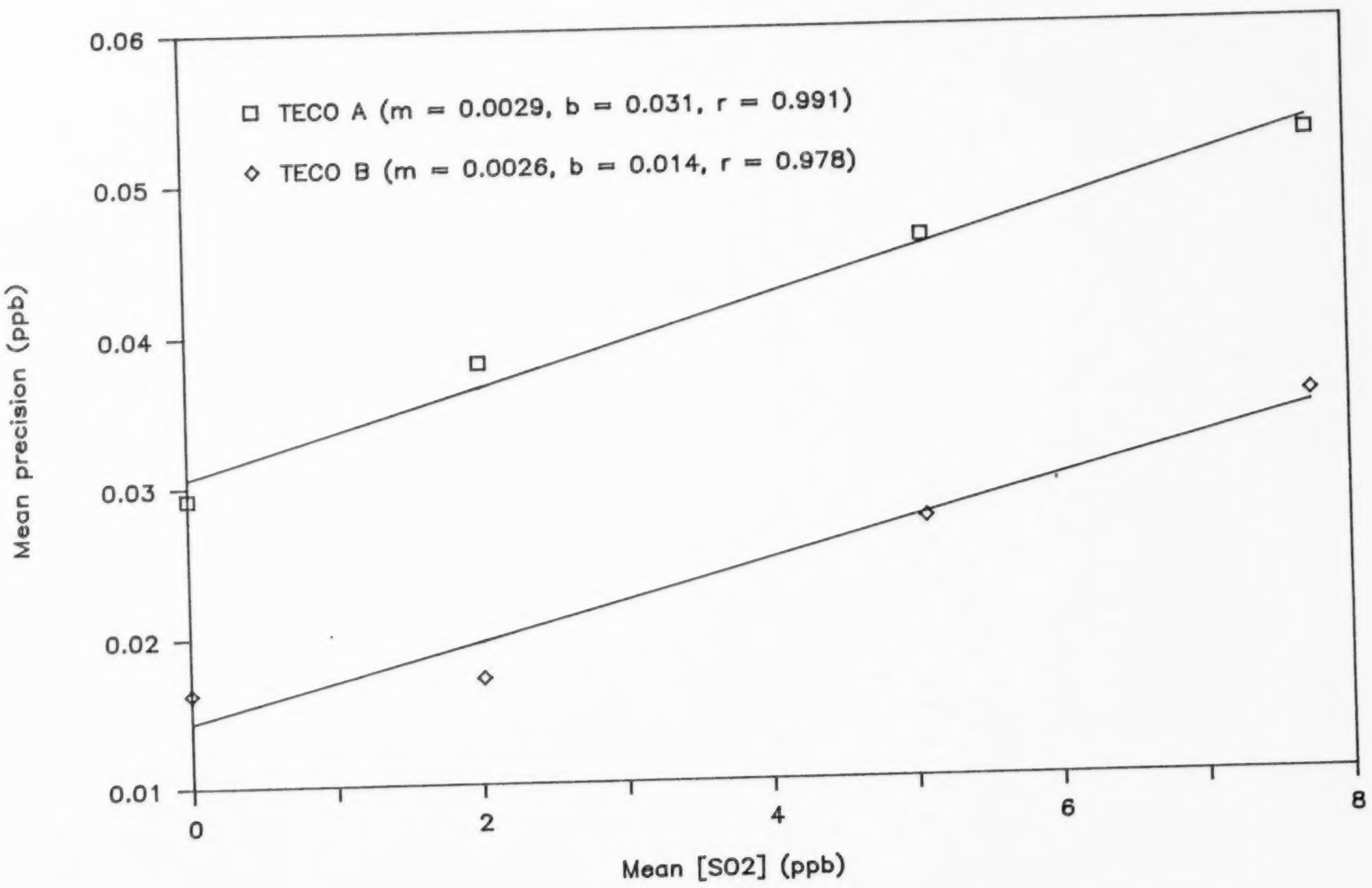

Figure 8. Mean precision versus concentration for TECO 43S SO_2 analyzers.

TABLE 23. REGRESSION OF MEAN PRECISION VERSUS AVERAGE CONCENTRATION FOR THERMO ENVIRONMENTAL MODEL 43S SO_2 ANALYZERS

Analyzer	Slope (ppb/ppb)	Intercept (ppb)	Std. Error of Intercept (ppb)	r^2
TECO A	0.0029	0.0306	0.0020	0.982
TECO B	0.0026	0.0143	0.0028	0.958

TABLE 24. REGRESSION OF MEAN PRECISION VERSUS CONCENTRATION FOR THERMO ENVIRONMENTAL MODEL 43S SULFUR DIOXIDE ANALYZERS (FORCED THROUGH MEAN ZERO-PERCENT VALUE)

Analyzer	Slope (ppb/ppb)
TECO A	0.00317
TECO B	0.00252

TABLE 25. DETECTION LIMITS FOR SULFUR DIOXIDE ANALYZERS

Performance Parameter	Units	TECO A	TECO B
Limit of Detection [a]	ppb	0.088	0.049
Limit of Detection [b]	ppb	0.088	0.049
Limit of Quantification	ppb	0.292	0.163
Limit of Quantification	ppb	0.302	0.167
Lower Detection Limit [e]	ppb	0.065	0.031
Lower Detection Limit [f]	ppb	0.059	0.033

[a] Limit of detection = 3 (mean precision at 0%)

[b] Limit of detection = 3(mean precision at 0%)/(1-3m) where m = the forced regression slope

[c] Limit of quantification = 10 (mean precision at 0%)

[d] Limit of quantification = 10(mean precision at 0%)/(1-10m)

[e] Lower detection limit = 2(mean noise at 0%)

[f] Lower detection limit = 2(mean noise at 0%)/(1-2m)

The zero drifts, as shown in Table 26, are presented in units of ppb. They are obtained from the morning and evening average zero noise measurements. They are calculated by multiplying the voltage shift from one day to the next by the next day's span factor (in units of ppb/volt). In general, the daily zero drifts are small and are consistent between the two analyzers and between the morning and evening measurements. It should be noted that most of the daily zero drifts are negative except for two large, positive values on Days 3 and 7. These two days in the test cycle are associated with the change from 105 to 125 volts and from 20 to 30 degrees Celsius. Accordingly, there is some evidence for temperature- and voltage-dependent zero drifts in the SO_2 analyzers.

It should be noted that the temperature shift for Day 5 is the reverse of those for Days 3 and 7. However, the zero drifts for Day 5 are not unusual.

Nine-day average zero drifts are also presented in Table 26. Their values approach zero which, on the surface, would indicate that no secular trends exist. However, if the data from Days 3 and 7 are excluded from the calculation, a secular trend becomes apparent. The revised average zero drift for both analyzers and for both morning and evening zero noise measurements is approximately -0.11 ppb/day or approximately -1.1 percent full scale/day. Overlaying this secular trend is a temperature- and voltage-dependent zero drift that is most evident on Days 3 and 7. The overnight zero drifts (Table 27) are similar to the daily zero drifts.

Daily span drifts are calculated from the mean values of the daily 20-, 50-, and 80-percent precision measurements. They are presented in units of percent. They are calculated from the relative shift of the mean precision value from one day to the next and are corrected for the slight day-to-day variations in the calibration concentrations. The daily span drifts are presented in Table 28. In general, they are small and are consistent between the two analyzers at each of the three concentration levels. It should be noted that most of the daily span drifts are negative except for large positive values on Days 3 and 7. These two days in the test cycle are associated with the change from 105 to 125 volts and from 20 to 30 degrees Celsius. Accordingly, there is some evidence for temperature- and voltage-dependent span drifts in the SO_2 analyzers. The span drifts in Table 28 are not corrected for the day-to-day variations in the zero levels.

The overall parameter that is used to evaluate any secular trends in the analyzers' spans is the average daily span drift across the nine-day test cycle. These values are also presented in Table 28. They approach zero which, on the surface, would indicate that no secular trends exist. However, a secular trend becomes apparent if the data from Days 3 and 7 are excluded from the calculation. The revised average span drifts for both analyzers are approximately -5.5 percent/day at the 20 percent full scale level, approximately -2.5 percent/day at the 50 percent full scale level and approximately -1.4 percent/day at the 80 percent full scale level. These revised average span drifts correspond to approximately -1.1, -1.3, and -1.1 percent full scale/day, respectively. These values are approximately equal to the revised average zero drifts. This observation strongly indicates that the zero drift has produced false signs of span drift in the SO_2 analyzers.

TABLE 26. DAILY ZERO DRIFTS FOR SULFUR DIOXIDE ANALYZERS ACROSS TEST DAYS

		Daily Zero Drift (ppb)			
		Morning		Evening	
Day	Conc	TECO A	TECO B	TECO A	TECO B
0	0%	NA	NA	NA	NA
1	0%	-0.092	-0.058	-0.073	-0.073
2	0%	-0.059	-0.115	-0.066	-0.095
3	0%	0.383	0.402	0.381	0.402
4	0%	-0.148	-0.175	-0.158	-0.165
5	0%	-0.132	-0.112	-0.136	-0.153
6	0%	-0.078	-0.101	-0.057	-0.066
7	0%	0.325	0.328	0.344	0.347
8	0%	-0.120	-0.148	-0.149	-0.172
Avg		0.010	0.003	0.011	0.003
Stdev		0.215	0.227	0.221	0.233
Max		0.383	0.402	0.381	0.402
Min		-0.148	-0.175	-0.158	-0.172
Revised Avg[a]		-0.105	-0.118	-0.106	-0.121
Revised Stdev[a]		0.034	0.040	0.046	0.048
Revised Max[a]		-0.059	-0.058	-0.057	-0.066
Revised Min[a]		-0.148	-0.175	-0.158	-0.172

[a] Excluding Days 3 and 7

TABLE 27. OVERNIGHT ZERO DRIFTS FOR SULFUR DIOXIDE ANALYZERS BETWEEN TEST DAYS

		Overnight Zero Drift (ppb)[a]	
Day	Conc %	TECO A	TECO B
0	0%	NA	NA
1	0%	-0.093	-0.057
2	0%	-0.080	-0.098
3	0%	0.369	0.399
4	0%	-0.160	-0.177
5	0%	-0.134	-0.124
6	0%	-0.076	-0.073
7	0%	0.306	0.322
8	0%	-0.159	-0.173
Avg		-0.003	0.002
Stdev		0.214	0.226
Max		0.369	0.399
Min		-0.160	-0.177
Revised Avg[b]		-0.117	-0.117
Revised Stdev[b]		0.039	0.050
Revised Max[b]		-0.076	-0.057
Revised Mins[b]		-0.160	-0.057

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[a] Overnight zero drift = (day n span factor) (overnight voltage shift)

[b] Excluding Days 3 and 7

TABLE 28. DAILY SPAN DRIFTS FOR SULFUR DIOXIDE ANALYZERS

		Daily Span Drift[a]			Daily Span Drift[a]	
Day	Conc	TECO A	TECO B	Conc	TECO A	TECO B
0	80%	NA	NA	50%	NA	NA
1	80%	0.7%	1.5%	50%	1.0%	1.2%
2	80%	-0.6%	-0.9%	50%	-1.8%	-2.5%
3	80%	5.3%	6.6%	50%	8.2%	9.8%
4	80%	-2.2%	-1.5%	50%	-3.4%	-2.9%
5	80%	-3.0%	-3.2%	50%	-2.7%	-3.5%
6	80%	-2.1%	-2.5%	50%	-5.0%	-3.3%
7	80%	7.1%	8.6%	50%	11.4%	10.5%
8	80%	-1.2%	-2.0%	50%	-4.2%	-3.8%
Avg		0.5%	0.8%		0.4%	0.7%
Stdev		3.7%	4.4%		6.1%	6.0%
Max		7.1%	8.6%		11.4%	10.5%
Min		-3.0%	-3.2%		-5.0%	-3.8%
Revised Avg[b]		-1.4%	-1.4%		-2.6%	-2.5%
Revised Stdev[b]		1.3%	1.6%		2.1%	1.9%
Revised Max[b]		0.7%	1.5%		1.0%	1.2%
Revised Min[b]		-3.0%	-3.2%		-5.0%	-3.8%

[a] Corrected for variations in SO_2 concentrations

[b] Excluding Days 3 and 7

(Continued)

TABLE 28. DAILY SPAN DRIFTS FOR SULFUR DIOXIDE ANALYZERS (Cont'd)

Day	Conc	Daily Span Drift[a]	
		TECO A	TECO B
0	20%	NA	NA
1	20%	-2.7%	1.9%
2	20%	-3.6%	-5.6%
3	20%	17.8%	18.8%
4	20%	-7.6%	-7.2%
5	20%	-8.4%	-8.8%
6	20%	-4.6%	-4.8%
7	20%	17.9%	17.8%
8	20%	-7.7%	-7.0%
Avg		0.1%	0.7%
Stdev		11.1%	11.3%
Max		17.9%	18.8%
Min		-8.4%	-8.8%
Revised Avg[b]		-5.8%	-5.2%
Revised Stdev[b]		2.4%	3.8%
Revised Max[b]		-2.7%	1.9%
Revised Min[b]		-8.4%	-8.8%

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[a] Corrected for variations in SO2 concentrations.
Excluding Days 3 and 7

To avoid complications associated with zero drift and to obtain a single parameter to assess the daily span drift, the span data are converted into the daily span factors presented in Table 29. The daily span factors are the slopes of the least-squares regression lines that are calculated from the mean daily precision values at zero-, 20-, 50-, and 80-percent of full scale range. The mean precision values fall very nearly onto a straight line. The coefficients of determination (r^2) for the regressions range from 0.9997 to 1.0000. The daily span factor drifts are calculated from the relative shift of the span factors from one day to the next. In general, the span factor drifts are consistent between the two analyzers. It should be noted that the span factor drift for Day 7 is the largest of the group. However, the span factor drift for Day 3 is small. Contrary to what was found for the span drifts, these data do not provide strong evidence for temperature or voltage effects.

The overall parameter that is used to evaluate any secular trends in the analyzers' span factors is the average daily span factor drifts across the nine-day test cycle. These values are small and do not suggest a secular trend to the span factor data. They are consistent between the two analyzers.

In summary, the results in this subsection for the zero and span drift tests can be interpreted as follows:

- There is a secular trend to the zero values;
- The zero values appear to have a temperature and voltage dependence;
- The zero drifts produce a noticable effect on the span drift values, which are not corrected for zero drift;
- The zero drifts do not produce a noticeable effect on the span factor drifts; and
- The span factors do not exhibit a noticeable secular trend or strong evidence for temperature and voltage dependence

Temperature and Voltage Effects on Drift

Temperature and voltage matrices for the zero values and span factors are given in Tables 30 and 31, respectively. The easiest way to evaluate whether temperature- or voltage-dependent drifts exist is to perform a simple linear regression involving only a single dependent variable (e.g. the zero values) and a single independent variable (e.g. the temperatures). This approach will be taken to evaluate the data in Tables 30 and 31. A more sophisticated approach would be to perform a multiple linear regression involving one dependent variable and three independent variables (i.e. temperature, voltage, and date).

Simple linear regression of the zero values suggests that the zero values are slightly dependent on temperature, but not on voltage. The results are consistent between the two analyzers and between the morning and evening measurements. The regression of zero values against temperature yielded slopes ranging from 0.023 to 0.026 ppb/°C and r^2 ranging from 0.73 to 0.84. The regression of zero values against voltage yielded slopes ranging from 0.005 to 0.007 ppb/volt and r^2 ranging from 0.13 to 0.25.

TABLE 29. SPAN FACTORS AND DAILY SPAN FACTOR DRIFTS FOR SULFUR DIOXIDE ANALYZERS

	Span Factors		Daily Span Factor Drift	
	TECO A	TECO B	TECO A	TECO B
Day	(ppb/V)	(ppb/V)	(percent)	(percent)
0	1.036	1.024	NA	NA
1	1.016	1.003	-2.0%	-2.1%
2	1.016	0.999	-0.1%	-0.3%
3	1.009	0.979	-0.7%	-2.0%
4	1.012	0.974	0.3%	-0.5%
5	1.022	0.987	1.0%	1.3%
6	1.040	1.004	1.7%	1.6%
7	1.005	0.955	-3.5%	-5.1%
8	1.001	0.958	-0.3%	0.3%
Avg	1.018	0.987	-0.4%	-0.9%
Stdev	0.013	0.023	1.7%	2.2%
Max	1.040	1.02	1.7%	1.6%
Min	1.001	0.955	-3.5%	-5.1%

[a] Determined from the slope of the linear regression of calibration data at zero, 20, 50 and 80 percent full scale.

TABLE 30. TEMPERATURE AND VOLTAGE MATRICES FOR SULFUR DIOXIDE ZERO VALUES

A) Morning zero values (in ppb) for TECO A

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 -0.129 Day 6 -0.104		Day 1 -0.070 Day 5 -0.026
25		Day 0 0.023	
30	Day 4 0.106 Day 8 0.101		Day 3 0.254 Day 7 0.221

B) Morning zero values (in ppb) for TECO B

deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 -0.126 Day 6 -0.111		Day 1 -0.011 Day 5 -0.010
25		Day 0 0.047	
30	Day 4 0.102 Day 8 0.070		Day 3 0.276 Day 7 0.218

(Continued)

TABLE 30. TEMPERATURE AND VOLTAGE MATRICES FOR SULFUR DIOXIDE ZERO VALUES (Cont'd)

C) Evening zero values (in ppb) for TECO A

	Temp	Line Voltage	
deg C	105 V AC	115 V AC	125 V AC
20	Day 2 -0.115 Day 6 -0.085		Day 1 -0.049 Day 5 -0.028
25		Day 0 0.024	
30	Day 4 0.108 Day 8 0.110		Day 3 0.266 Day 7 0.260

D) Evening zero values (in ppb) for TECO B

Temp	Line Voltage		
deg C	105 V AC	115 V AC	125 V AC
20	Day 2 -0.123 Day 6 -0.104		Day 1 -0.027 Day 5 -0.038
25		Day 0 0.046	
30	Day 4 0.114 Day 8 0.071		Day 3 0.279 Day 7 0.243

TABLE 31. TEMPERATURE AND VOLTAGE MATRICES FOR SULFUR DIOXIDE SPAN FACTORS

A) Span factors for TECO A (ppb/volt)

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 1.016 Day 6 1.040		Day 1 1.016 Day 5 1.022
25		Day 0 1.036	
30	Day 4 1.012 Day 8 1.001		Day 3 1.009 Day 7 1.005

B) Span factors for TECO B (ppb/volt)

Temp deg C	Line Voltage		
	105 V AC	115 V AC	125 V AC
20	Day 2 0.999 Day 6 1.004		Day 1 1.003 Day 5 0.987
25		Day 0 1.024	
30	Day 4 0.974 Day 8 0.958		Day 3 0.979 Day 7 0.955

The temperature shift on Days 3 and 7 was 10°C. The slopes of the zero value-against-temperature regressions would predict a zero shift of 0.23 to 0.26 ppb as the result of such a temperature shift. These predictions are similar to the observed zero drifts on Days 3 and 7. The corresponding predicted zero shift for Day 5 is 0.23 to 0.25 ppb. This zero shift was not observed on Day 5.

The effect of any secular trends in the drift data is reduced because the measurement at each set of temperatures and voltages are repeated twice. Nevertheless, it is still possible for a secular trend to affect the regression estimates.

Simple linear regression of the span factors suggest that the span factors are not dependent on either temperature or voltage. The results are consistent between the two analyzers. The regression of span factors against temperature yielded slopes of -0.002 and -0.003 ppb/°C and r^2 of 0.40 and 0.49. The regression of span factors against voltage yielded slopes of 0.000 and 0.001 ppb/volt and r^2 of 0.00 and 0.17.

In summary, the SO_2 analyzers exhibit a slight temperature-dependent zero drift. The span factors are not dependent on either temperature or voltage.

Response Time

The rise and fall times for the TECO 43S SO_2 analyzers are presented in Tables 32 and 33, respectively. The rise and fall times are consistent from day-to-day. Their mean values are approximately equal. It should be noted that these values may include delays associated with conditioning the PFA Teflon^{TM} walls of the calibration apparatus.

The TECO 43S SO_2 analyzers took long periods of time (i.e., approximately 2 hours) to rise from approximately 95 to 100 percent of their final, stable readings during each test day's initial change from an overnight zero air exposure to an 80-percent full scale concentration. This phenomenon was not observed after subsequent step concentration changes during each test day. It is hypothesized to be associated with the daily initial conditioning of the calibration apparatus and the sample lines after the overnight zero air exposure.

Interferences

The results of the interference tests are presented in Table 34. The interference tests were conducted in the presence of a SO_2 concentration approximately equal to 50 percent (i.e. 5 ppb) of the full-scale range. An analyzer is considered to have a measurable response to a given interferent if the difference between the response with and without the interferent exceeded the 95% confidence limits for the analyzer's response at 50% concentration. These limits were obtained by multipling 1.96 times the precision at 50% concentration (Table 22). The results are discussed in separate sections by interferent below.

TABLE 32. RISE TIMES FOR SULFUR DIOXIDE ANALYZERS

Day	Test	TECO A (min)	TECO B (min)
0	1	3.4	3.5
0	2	3.7	3.6
0	3	3.2	3.3
1	1	3.5	3.5
1	2	3.3	3.1
1	3	3.4	3.2
2	1	3.3	3.2
2	2	3.6	3.1
2	3	3.7	3.3
3	1	2.8	3.1
3	2	3.8	3.7
3	3	3.5	3.3
4	1	3.7	3.6
4	2	3.8	3.5
4	3	3.4	3.2
5	1	3.5	3.2
5	2	3.3	3.3
5	3	3.3	3.2
6	1	3.7	3.4
6	2	3.8	3.5
6	3	3.3	3.7
7	1	3.7	3.6
7	2	3.7	3.6
7	3	3.9	3.3
8	1	3.3	3.3
8	2	3.7	3.2
8	3	3.7	3.4
Avg		3.5	3.4
Stdev		.2	.2
Max		3.9	3.7
Min		2.8	3.1

TABLE 33. FALL TIMES FOR SULFUR DIOXIDE ANALYZERS

Day	Test	TECO A (min)	TECO B (min)
0	1	3.3	3.6
0	2	3.2	3.2
0	3	3.1	3.1
1	1	3.4	3.3
1	2	3.5	3.8
1	3	3.5	3.5
2	1	3.1	3.2
2	2	3.2	3.4
2	3	3.6	3.3
3	1	3.9	3.5
3	2	3.7	3.6
3	3	3.6	3.5
4	1	3.6	3.6
4	2	3.3	3.4
4	3	3.4	3.5
5	1	3.2	3.6
5	2	3.5	3.5
5	3	3.6	3.5
6	1	3.5	3.4
6	2	3.1	3.4
6	3	3.0	3.3
7	1	3.4	3.3
7	2	3.7	3.6
7	3	3.6	3.6
8	1	3.5	3.5
8	2	3.5	3.8
8	3	3.6	3.6
Avg		3.4	3.5
Stdev		.2	.2
Max		3.9	3.8
Min		3.0	3.1

TABLE 34. INTERFERENCE TEST RESULTS FOR SULFUR DIOXIDE ANALYZERS

Species	[Species] (ppb)	$[SO_2]$ (ppb)	Change in $[SO_2]$ TECO A (ppb)	Change in $[SO_2]$ TECO B (ppb)	Relative Response = change in $[SO_2]$ (ppb)/[interferent] (ppb) TECO A	Relative Response TECO B	Notes
O_2	-2.1E+08	5.12	4.80	5.15	-2.3E-08	-2.5E-08	1
O_2	1.6E+08	5.12	ND	ND	ND	ND	2
CO_2	7.5E+05	5.12	ND	ND	ND	ND	3
NO	1.3E+02	5.12	3.81	2.96	2.8E-02	2.1E-02	
H_2S	1.2E+02	5.12	0.12	0.12	9.8E-04	1.0E-03	
H_2O	1.3E+07	5.12	ND	-0.09	ND	-7.1E-09	
Xylene	3.2E+02	5.10	3.10	2.61	1.0E-02	8.1E-03	

ND = Change in $[SO_2]$ is less than the 95% confidence limits based on 1.96 times the standard deviation at a concentration of 50% of full scale.
Key to exponential notation: -2.1E +08 is equivalent to $-2.1 \times 10^{+08}$

Notes:

1. N_2 used as dilutant in place of zero air. Change is relative to zero air.

2. 37 percent O_2 in N_2 was used as the dilutant. Change is relative to zero air.

3. CO_2 concentration is that of spike above the CO2 present in zero Air.

Oxygen --

Oxygen (O_2) interference was tested by replacing the dilutant zero air ($[O_2]$ approximately 21%) with dilutants of pure nitrogen and nitrogen containing higher than ambient concentrations of O_2. First, when pure nitrogen ($[O_2] = 0\%$) was used as a dilutant, a measurable response was seen. Second, when a mixture of 37% O_2 in nitrogen was used as an interferent, no measurable interference was seen. This indicates that no O_2 interference is likely to be seen during calibration if either filtered ambient air or compressed synthetic zero air is used to prepare calibration mixtures.

Carbon Dioxide --

No carbon dioxide interference was detected.

Nitric Oxide --

The TECO 43S SO_2 analyzers showed measurable interference to nitric oxide (NO). The magnitude of the relative interference response was 0.028 ppb SO_2/ppb NO for TECO A and 0.021 ppb SO_2/ppb NO for TECO B. Using the relative interference response for each analyzer, the detection limit for NO as SO_2 at 0% SO_2 concentration is between 2 and 3 ppb NO. This level could be reasonably expected at all but the most isolated site locations. Whether the NO interference would be significant would depend both on the NO level expected at the monitoring site and the needs of the user. It is recommended that NO concentrations at sites using this analyzer be monitored so the interference problems from NO can be measured. The SO_2 measurements by the TECO 43S analyzer can then be corrected for the NO interference. As will be discussed later, the SO_2 data from the field evaluation were corrected for the NO interference.

Equivalency testing data supplied by Thermo Electron Co. for their model 43A SO_2 analyzer (F. McElroy, EPA, personal communication) indicate a nitric oxide interference level of approximately 2 ppb at a NO concentration of approximately 500 ppb. This corresponds to a relative response of 4×10^{-3} ppb SO_2 response per ppb NO or roughly one-sixth the relative interference seen in the TECO 43S SO_2 analyzer. The increase in interference seen by the more sensitive model 43S may be due to changes in the optical filter bandwidth, which were made to improve the analyzer's sensitivity relative to that of the TECO 43A SO_2 analyzer.

Hydrogen Sulfide --

Measurable response to hydrogen sulfide (H_2S) was seen in both analyzers. It should be noted that it is possible that a small amount of SO_2 could have been present from oxidation of H_2S in the cylinder or manifold. However, regardless of whether the response was due to H_2S or due to possible low-level present of SO_2 in the H_2S, the SO_2 response was not sufficiently large for H_2S interference to be a problem at most locations. Whether the H_2S interference would be significant would depend both on the H_2S level expected at the monitoring site and the needs of the user. Care should be exercised to avoid locating analyzers near potential H_2S sources until further studies of H_2S interference can be performed.

Water --

Measurable water interference was seen on only one of the two analyzers. For a "worst-case" estimate of the impact that water interference would have on analyzer response, consider a change from 10% relative humidity to 80% relative humidity at 100 degrees Fahrenheit (37 degrees C). This corresponds to a change in the water concentration of 34 Torr or 4.5 x 10^7 ppbv. This would result in a change for the one analyzer which saw a measurable interferent response of approximately 0.3 ppb at a concentration of 5 ppb or a 6% error.

Xylene --

Possible interference to aromatic and conjugated hydrocarbons was tested using xylene as a model interferent. Measurable interference to xylene was seen on both analyzers. Using the average relative interferent response of 0.009 ppb SO_2/ppb xylene, the detection limit for xylene as SO_2 at 0% SO_2 concentration would be between 5 and 10 ppb xylene. Whether the aromatic hydrocarbon interference would be significant would depend both on the aromatic hydrocarbon level expected at the monitoring site and the needs of the user.

Equivalency testing data supplied by Thermo Electron Co. for their model 43A SO_2 analyzer (F. McElroy, EPA, personal communication) indicate a m-xylene interference level of approximately 1.7 ppb at a m-xylene concention of approximately 200 ppb. This corresponds to a relative response of 8.5 x 10^{-3} ppb SO_2 response per ppb m-xylene or roughly the same level of relative response seen in the TECO 43S SO_2 analyzer.

FIELD EVALUATION OF EXTRASENSITIVE ANALYZERS

Maintenance and Operational Failures

The TECO 43S SO_2 analyzers required no maintenance during the field evaluation. The CSI 1600 NO_2 analyzers only required replacement of the dessicant (Drierite TM) used on their ozonator intake line. This is part of normal maintenance for this model. The zero and span pots for the CSI 1600 and TECO 43S analyzers were not adjusted during the field evaluation. They remained at the same settings as during the laboratory evaluation. Normal LMA 3 maintenance included replenishment of luminol solution and replacement of pump tubing at approximately two week intervals during the field evaluation (i.e. on April 25 and on May 9 and 23).

In general, zero and span pots on the LMA 3 analyzers were not adjusted when the luminol solution and the pump tubing were replaced (which always were done at the same time). Only luminol from the same lot number (871103) was used in both laboratory and field evaluations. The effect of variations in luminol solution was not tested in this project.

The LMA 3 analyzers were backflushed on a daily basis during the field evaluation. Backflushing was done immediately after the zero and span checks until May 7 (Julian Day 128) and was done immediately before the zero and span checks following that date. This change in the time that the backflushing occurred removed an instability in LMA B's response that had been seen during the span checks. Backflushing did not shift the LMA 3 analyzers' span factors.

As will be discussed in the next subsection, span factor shifts were observed for LMA B on May 9 and 23 (Julian Days 130 and 144) when the pump tubing was replaced. The span factor shift of May 9th was large enough to require a span pot adjustment. Similar shifts were not observed for LMA A. It is hypothesized that excessive wear was occurring in LMA B's pump tubing. This same analyzer had pump tubing problems during the laboratory evaluation.

One LMA 3 analyzer (LMA A) had luminol solution sucked back out of the reaction cell and into the ozone trap on Apr. 26 (Julian day 117). This clogged the trap which necessitated trap replacement. The analyzer (LMA A) was operated without an ozone trap until May 2 (Julian day 123), when a replacement was obtained.

On April 26 and 27 (Julian Days 117 and 118), the air pump tubing fell off of LMA B. Ten hours of the LMA B's data were lost as a result of this failure.

Several of the trailer's ambient air quality monitors failed on various occasions during the field evaluation. The trailer's NO_x analyzer displayed excessive zero and span drift during the early part of the field evaluation. It was replaced with another analyzer of the same model on May 11 (Julian Day 132). All data collected by this analyzer before May 12 (Julian Day 133) has been discarded. The trailer's SO_2 instrument did not collect valid data from 1000 EST, May 16 (Julian Day 137) to 1100 EST on the following day because its sampling line was not connected to the sample manifold.

The trailer's air conditioner failed during the multipoint calibration of May 10 (Julian Day 131). The temperature inside the trailer reached 32 degrees Celsius. A thermometer placed on top of one CSI 1600 analyzer measured 35 degrees Celsius. The NO_x channel of CSI A temporarily malfunctioned and produced a large output voltage that was independent of the input concentration. Many of the analyzers displayed significant zero or span shifts as a result of the high temperature. All data for this day have been discarded.

A power failure on May 16 (Julian Day 137) of approximately 2 minutes duration caused temporary disruption of analyzer operation, but there was no significant loss of data for the extrasensitive analyzers. The trailer's O_3 and dewpoint instruments lost data for several hours.

There was an extremely brief power failure on May 20 (Julian day 141), with a duration long enough to cause failure of the station's dewpoint sensor but insufficient to disrupt the computer-based data acquisition system. No extrasensitive-analyzer data was affected.

Data were lost on several occasions due to maintenance to or problems with the trailer's data acquisition system. The periods of missing data are as follows:

- 1400 EST, May 4 (Julian Day 125);
- 1400 EST, May 8 (Julian Day 129) through 0400 EST, May 9 (Julian Day 130)
- 1500 EST, May 17 (Julian Day 138) through 1100 EST, May 18 (Julian Day 139);
- 0600 EST, May 19 (Julian Day 140)

Zero and Span Factor Drift

Over the course of the field evaluation, 3 multi-point calibrations and 21 zero and span checks were performed. The multi-point calibrations took place at the beginning, middle, and end of the field evaluation. Data from the multipoint calibrations are discussed in the next subsection. Zero and span checks took place on a daily basis from April 26th through May 12th and on a bi-daily basis from May 14th through May 24th. The data from these calibrations are used to evaluate the zero and span drift characteristics of the extrasensitive analyzers.

The zero and span voltages are 30-minute averages of voltages that were collected at 30-second intervals by the Fluke Model 2240C Data Logger.

Zero values for the field evaluation are presented in Table 35 and in Figures 9 through 11. They are given in units of ppb. They are calculated by multiplying the differences between the daily mean zero voltages and the overall mean zero voltages by the mean span factors for the field evaluation. This computational approach allows the zero values of the extrasensitive analyzers to be compared on a meaningful basis. A comparison of the zero voltages would not be meaningful.

The NO_2 zero values for CSI B are anomalously high on April 26 and 27 (Julian Days 117 and 118). It is hypothesized that this analyzer was restabilizing after its transport from the laboratory to the trailer.

As noted above, the trailer's air conditioner failed on May 10 (Julian Day 131). All three models of the extrasensitive analyzers exhibited noticeable shifts in their zero values as a result of the failure. CSI A was the most seriously affected. Its NO_x channel had a high value independent of the NO_x concentration. An electronic failure is suspected as the cause. All the extrasensitive analyzers had restabilized by the following day's zero and span check after the air conditioner had been repaired.

A statistical analysis of the zero values is also presented in Table 35. The average zero values equal 0.000 ppb as a result of the approach that was used to calculate the zero values. The standard deviations of the zero values are consistent between the two analyzers of each analyzer model. The standard deviations for the LMA 3 analyzers are lower than those of the CSI 1600 analyzers.

A qualitative review of the NO_2 zero values does not indicate any secular trends for the CSI 1600 and LMA 3 analyzers. The zero values for the TECO 43S analyzers appear to have a general downward trend over the period of the field evaluation. Simple linear regression of these zero values against the Julian date for the period from Day 117 through Day 130 suggests slight secular trends. For TECO A, the regression has a slope of -0.011 ppb/day with a r^2 of 0.62. For TECO B, the regression has a slope of -0.008 ppb/day with a r^2 of 0.71. It should be noted that these slopes are approximately an order of magnitude less than the secular trends (i.e., approximately -0.11 ppb/day excluding days 3 and 7) that were observed during the laboratory evaluation.

TABLE 35. FIELD EVALUATION ZERO VALUES

			Zero Value (ppb)[a]					
			TECO 43S SO_2		LMA 3 NO_2		CSI 1600 NO_2	
Month	Day	Julian Date	A	B	B	A	B	A
4	26	117	0.1242	0.0802	0.0250	-0.0091	0.6447	0.1685
4	27	118	0.0984	0.0773	0.0447	-0.0013	0.8398	0.2202
4	28	119	0.0169	0.0324	-0.0143	-0.0091	-0.1148	-0.0177
4	29	120	0.0283	0.0372	-0.0537	-0.0169	-0.1559	-0.2090
4	30	121	0.0623	-0.0179	-0.0635	-0.0169	0.0289	-0.1004
5	1	122	0.0355	0.0276	-0.0537	-0.0169	-0.1200	-0.1159
5	2	123	0.0242	0.0113	-0.0537	-0.0169	-0.2021	-0.0177
5	3	124	0.0221	-0.0011	0.0152	0.0221	0.0802	-0.0073
5	4	125	0.0077	-0.0116	0.0545	0.0065	0.0597	0.0547
5	5	126	-0.0356	-0.0393	0.0250	0.0143	-0.3099	0.0030
5	6	127	-0.0835	-0.0240	0.0348	-0.0013	-0.2945	-0.0952
5	7	128	-0.0655	-0.0403	0.0053	0.0065	-0.2585	-0.1263
5	8	129	-0.0253	-0.0336	-0.0143	-0.0013	-0.2996	-0.0332
5	9	130	0.0128	-0.0049	-0.0143	-0.0013	-0.1302	0.0082
5	10	131	0.0871	0.0706	0.2020	0.0533	-0.0173	0.2874[b]
5	11	132	0.0169	0.0123	-0.0242	-0.0169	-0.0225	0.0185
5	12	133	0.0056	0.0190	-0.0537	-0.0013	-0.1456	0.0030
5	14	135	-0.0150	-0.0020	-0.0242	-0.0013	0.0699	0.0702
5	16	137	-0.0161	-0.0298	0.0250	0.0065	0.0135	0.0030
5	18	139	-0.0594	-0.0202	-0.0242	0.0065	0.0802	-0.0539
5	20	141	-0.0635	-0.0279	0.0250	-0.0013	0.2701	-0.0332
5	22	143	-0.0604	-0.0260	0.0053	0.0065	0.1520	-0.0177
5	24	145	-0.0893	-0.0537	-0.0143	0.0065	0.0494	0.1582
5	26	147	-0.0284	-0.0355	-0.0537	-0.0169	-0.2175	-0.1676
Avg			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Std Dev			0.0568	0.0382	0.0555	0.0157	0.2766	0.1178
Max			0.1242	0.0802	0.2020	0.0533	0.8398	0.2874
Min			-0.0893	-0.0537	-0.0635	-0.0169	-0.3099	-0.2090

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[a] Zero values were calculated by multiplying the difference between the daily mean zero voltages and the overall mean zero voltage by the mean span factors for the field evaluation.

[b] The zero value for CSI A on Day 131 was calculated from the y-intercept of the linear regression of the multi-point calibration data.

(Continued)

TABLE 35. FIELD EVALUATION ZERO VALUES (Cont'd)

			Zero Value (ppb)[a]			
			CSI A		CSI B	
Month	Day	Julian Day	NO_x	NO	NO_x	NO
4	26	117	0.2161	0.1343	0.2166	-0.3913
4	27	118	0.5101	0.3715	0.7840	-0.0130
4	28	119	-0.3618	-0.2628	-0.6802	-0.5446
4	29	120	-0.2638	0.0312	-0.2039	-0.0232
4	30	121	-0.1503	0.0208	-0.1381	-0.1357
5	1	122	-0.1915	0.0054	-0.1279	0.0177
5	2	123	-0.0522	0.0518	-0.1735	0.0586
5	3	124	-0.0780	0.0105	0.1862	0.1404
5	4	125	0.1613	0.0827	0.3534	0.3244
5	5	126	-0.1606	-0.0823	0.0443	0.3857
5	6	127	-0.2122	-0.0359	-0.2901	0.0279
5	7	128	-0.2638	-0.0565	-0.2951	0.0079
5	8	129	-0.2070	-0.0875	-0.3154	0.0075
5	9	130	-0.1090	-0.0359	-0.1381	0.0228
5	10	131	1.9238[b]	-0.2267	0.4091	-0.2481
5	11	132	-0.3102	-0.2422	-0.0519	0.0023
5	12	133	-0.2277	-0.1545	-0.1786	-0.0130
5	14	135	-0.0884	-0.0823	0.0139	-0.0283
5	16	137	0.0974	0.1807	0.1710	0.1864
5	18	139	-0.1812	-0.0462	-0.0165	-0.0641
5	20	141	-0.1657	-0.0617	0.1963	-0.0437
5	22	143	-0.0161	0.0827	0.2875	0.1710
5	24	145	0.2883	0.2116	0.1203	0.0995
5	26	147	-0.0574	0.1910	-0.1735	0.0688
Avg			0.0000	0.0000	0.0000	-0.0000
Std Dev			0.4563	0.1509	0.3007	0.1972
Max			-0.3618	-0.2628	-0.6802	-0.5446
Min			1.9238	0.3715	0.3715	0.3857

[a] Zero values were calculated by multiplying the difference between the daily mean zero voltages and the overall mean zero voltage by the mean span factors for the field evaluation.

[b] The zero value for CSI A on Day 131 was calculated from the y-intercept of the linear regression of the multi-point calibration data.

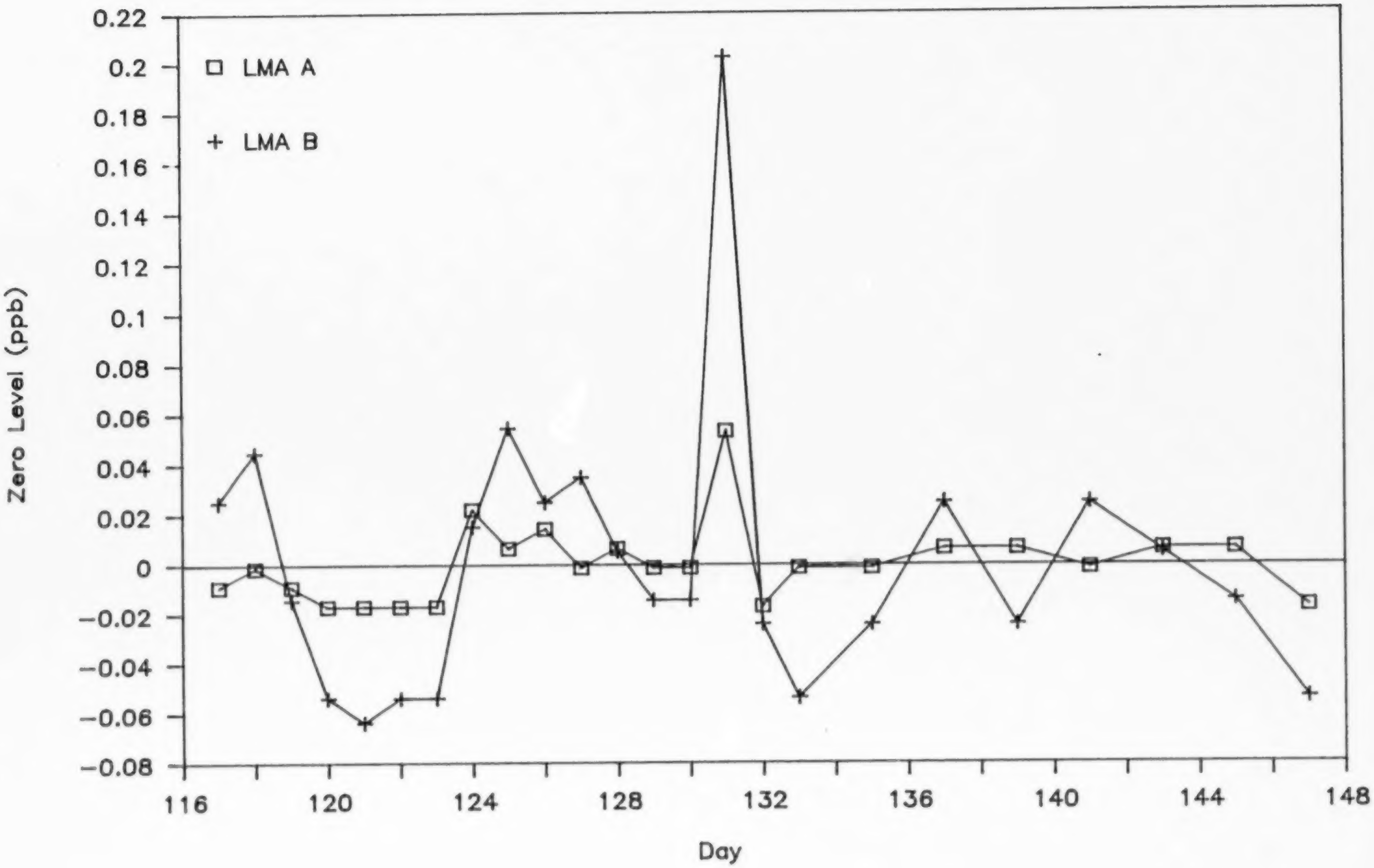

Figure 9. Zero values during the field evaluation for LMA 3 NO_2 analyzers.

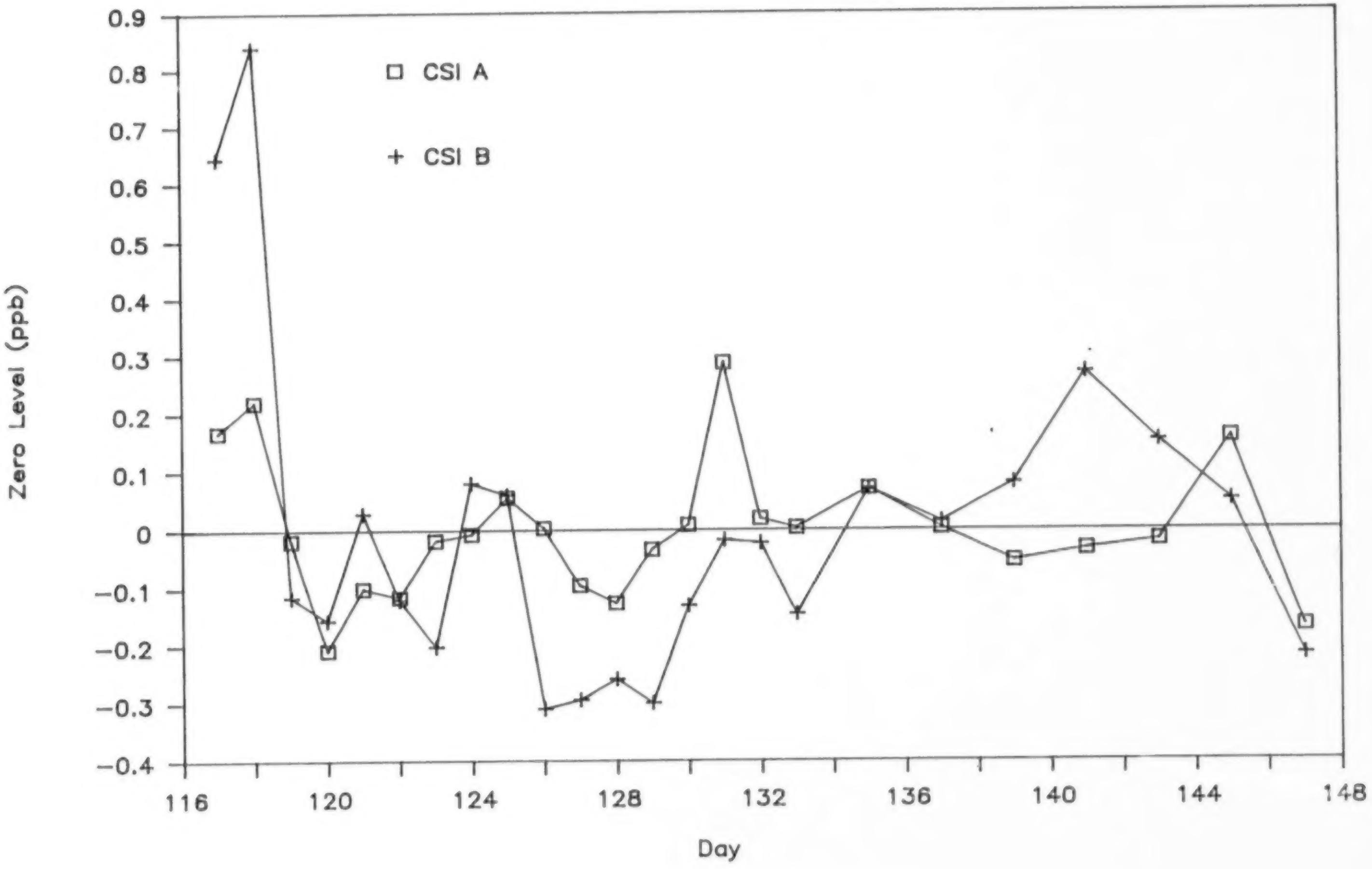

Figure 10. Zero values during the field evaluation for CSI 1600 NO_2 analyzers.

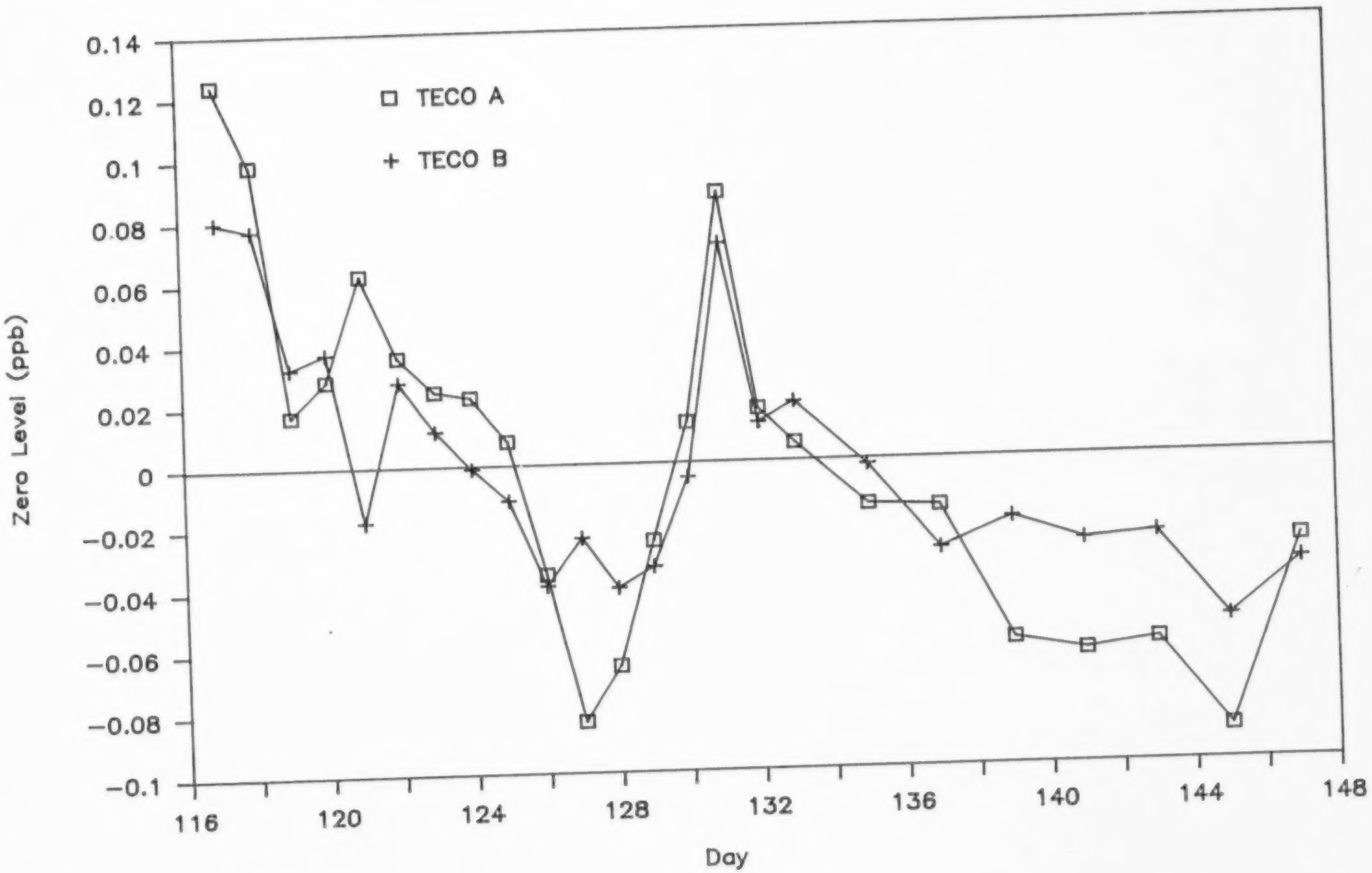

Figure 11. Zero values during the field evaluation for TECO 43S SO_2 analyzers.

Span factors for the field evaluation are presented in Table 36 and in Figures 12 through 14. They are given in units of ppb/volt. They are calculated from the concentrations and analyzer responses for the zero and 80% span checks except for May 10 (Julian Day 131) where the CSI A zero and span factors are calculated from the regression of the multi-point calibration data. Because the SO_2 and NO_2 analyzers were calibrated simultaneously, the SO_2 span factors take the NO interference into account by the following formula:

$$SO_2 \text{ span factor} = \left[\frac{[SO_2] + [NO][NO \text{ relative response}]}{[\text{Span voltage} - \text{zero voltage}]}\right]$$

where the NO relative response is taken from the laboratory evaluation's interference test.

As noted above, the trailer's air conditioner failed on May 10 (Julian Day 131). All three models of the extrasensitive analyzers exhibited noticeable shifts in their span factors in response to the failure. The CSI 1600 analyzers were the most seriously affected. The CSI 1600 and the LMA 3 analyzers had restabilized by the following day's zero and span check after the air conditioner had been repaired. The TECO 43S analyzers may have required two additional days for their span factors to restabilize after the failure.

A statistical analysis of the span factors is also presented in Table 36. The standard deviations of the span factors are consistent between the two analyzers of each analyzer model except for the LMA 3 analyzers. The standard deviation of the LMA B's span factors is 10.15% versus the corresponding value of 3.85% for LMA A. The standard deviations for the CSI 1600 analyzers are lower than those of the LMA 3 analyzers.

A qualitative review of the NO_2 span factors for the CSI 1600 analyzers and for LMA A does not indicate that secular trends exist in these span factors.

A qualitative review of the span factors for LMA B suggests a strong secular trend. During the intervals between the pump tubing changes on May 9 and 23 (Julian Days 130 and 144), the LMA B's span factors show a steady increase. Simple linear regression of these span factors against the Julian date supports this observation. For Days 117 through 129, the regression has a slope of 0.1813 ppb/volt-day with a r^2 of 0.70. For Days 130 through 143, the regression has a slope of 0.2740 ppb/volt-day with a r^2 of 0.91. For Days 145 through 147, the regression has a slope of 0.1815 ppb/volt-day with a r^2 of 1.00 (by definition). A time-weighted mean slope of 0.2166 ppb/volt-day is obtained from these slopes. Relative to the mean LMA B span factor of 9.83 ppb/volt, the mean slope corresponds to a span factor drift of 2.2%/day. It is hypothesized that this drift was caused by excessive wear in LMA B's pump tubing. The drift cannot be attributed to decay in the luminol solution because span factor drift was not observed in LMA A. It should be noted that span factor drift in the LMA 3 analyzers was not observed during the laboratory evaluation.

TABLE 36. FIELD EVALUATION SPAN FACTORS

			Span Factor = Concentration /voltage (ppb/V)					
			Teco 43S SO2[a]		LMA 3 NO_2		CSI 1600 NO_2	
Month	Day	Julian Day	A	B	B	A	B	A
4	26	117	1.071	1.022	8.857	7.375	55.35906	53.74339
4	27	118	1.046	1.007	9.532	8.174	55.17457	53.40480
4	28	119	1.027	0.971	8.536	7.557	51.30962	50.39029
4	29	120	1.066	0.997	8.996	7.692	52.75925	51.51703
4	30	121	1.037	0.962	9.081	7.478	50.42923	50.41424
5	1	122	1.048	0.973	9.636	7.611	50.89790	50.74694
5	2	123	1.044	0.970	10.056	7.501	50.20608	51.55636
5	3	124	1.021	0.956	9.637	7.851	49.69825	50.08083
5	4	125	1.066	0.983	10.938	8.097	52.01362	52.83823
5	5	126	1.039	0.965	10.573	8.041	51.14059	51.62809
5	6	127	1.049	0.975	11.274	8.009	51.11036	52.59727
5	7	128	1.010	0.938	10.309	7.530	50.66076	50.55983
5	8	129	1.026	0.956	10.476	7.749	51.40818	50.51968
5	9	130	1.037	0.968	7.903	7.601	50.89821	50.92147
5	10	131	1.003	0.929	8.370	7.064	48.69215	46.08756[b]
5	11	132	0.998	0.921	9.283	7.905	51.68479	52.17970
5	12	133	1.019	0.940	9.156	7.753	51.08838	51.54742
5	14	135	1.033	0.952	10.307	8.115	50.93319	53.69264
5	16	137	1.031	0.940	10.700	8.018	52.22815	53.64607
5	18	139	1.026	0.940	10.348	8.061	51.19392	53.13768
5	20	141	1.016	0.927	11.168	8.123	50.18261	52.28421
5	22	143	1.020	0.925	11.921	8.299	51.17455	53.85320
5	24	145	1.002	0.918	9.308	7.881	51.67037	52.34458
5	26	147	1.014	0.914	9.671	7.666	49.83956	51.45827
Avg			1.031	0.956	9.83	7.80	51.32	51.71
Std Dev			0.020	0.029	1.00	0.30	1.49	1.70
Rel St Dev			1.95%	2.98%	10.15%	3.85%	2.90%	3.29%
Max			1.07	1.02	11.92	8.30	55.36	53.85
Min			1.00	0.91	7.90	7.06	48.69	46.09

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[a] TECO 43S Span factors have been adjusted for interference due to NO present in field calibration mixtures.

[b] This span factor is the slope of the regression line for the multi-point calibration data.

(Continued)

TABLE 36. FIELD EVALUATION SPAN FACTORS (Cont'd)

			Span Factor (ppb/volt)			
			CSI A		CSI B	
Month	Day	Julian Day	NO_x	NO	NO_x	NO
4	26	117	52.752	53.368	54.058	55.276
4	27	118	52.681	52.398	53.760	54.340
4	28	119	49.892	50.110	50.497	51.073
4	29	120	51.551	51.629	51.696	52.839
4	30	121	50.363	50.094	50.205	50.310
5	1	122	50.583	50.376	50.412	50.785
5	2	123	51.213	50.786	50.628	50.798
5	3	124	49.975	49.603	49.356	49.408
5	4	125	52.351	52.130	51.294	51.544
5	5	126	51.612	51.086	50.205	51.140
5	6	127	52.205	51.983	50.873	51.509
5	7	128	51.224	50.387	49.822	49.463
5	8	129	51.360	51.571	49.916	50.554
5	9	130	51.877	51.653	50.066	50.739
5	10	131	47.978[a]	48.585	48.010	45.569
5	11	132	52.605	52.345	50.876	51.612
5	12	133	52.017	52.090	50.415	50.713
5	14	135	53.482	53.387	50.286	51.285
5	16	137	53.485	53.574	51.622	52.202
5	18	139	52.617	53.108	51.000	51.841
5	20	141	51.457	51.877	50.104	50.595
5	22	143	52.396	52.969	50.449	51.598
5	24	145	51.833	51.999	50.593	51.663
5	26	147	50.770	50.546	49.804	49.930
Avg			51.595	51.569	50.665	51.116
Std Dev			1.248	1.302	1.249	1.783
Rel Std			2.42%	2.53%	2.47%	3.49%
Max			53.485	53.574	54.058	55.276
Min			47.978	48.585	48.010	45.569

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[a] This span factor is the slope of the regression line for the multipoint calibration data.

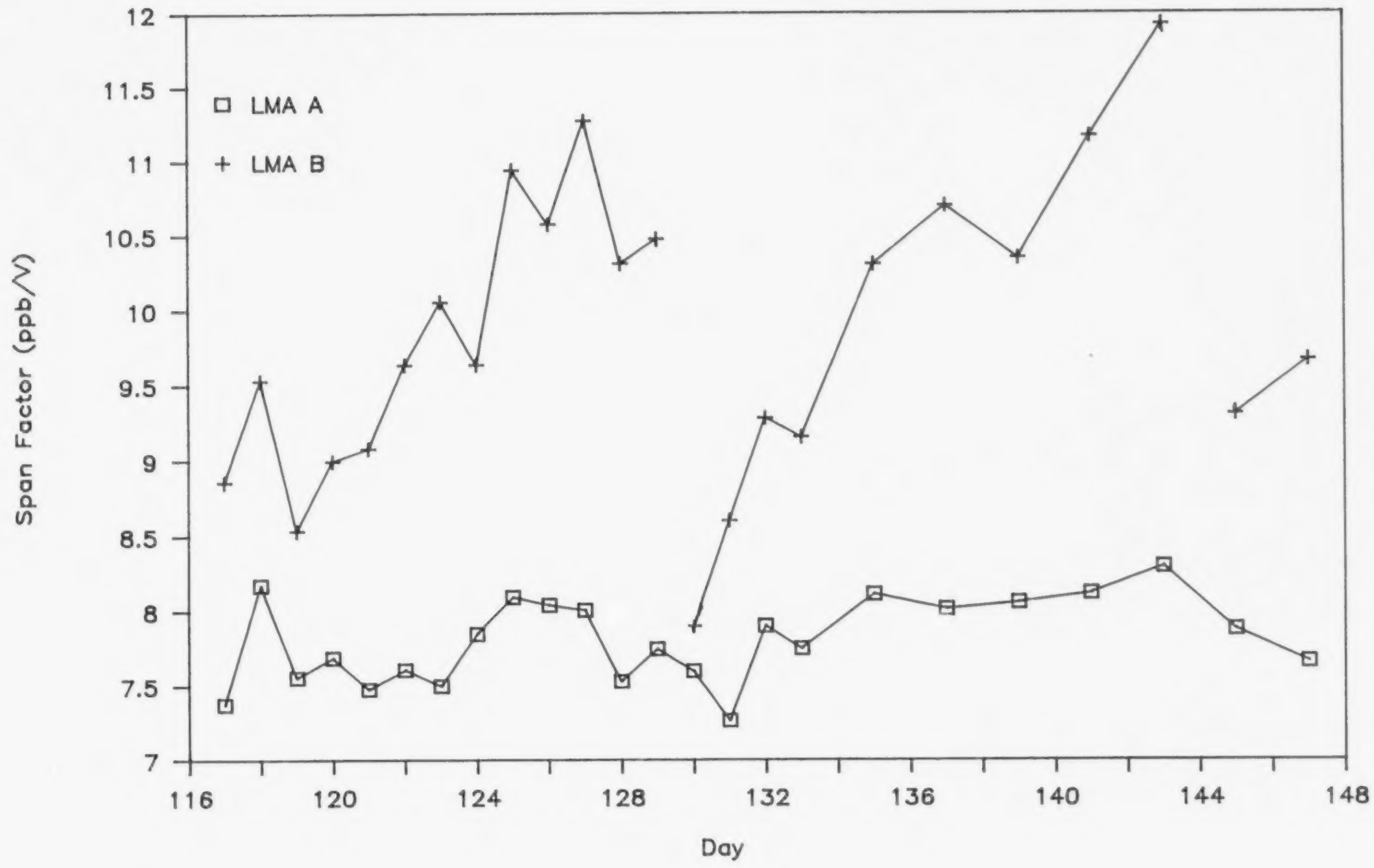

Figure 12. Span factors during the field evaluation for LMA 3 NO_2 analyzers.

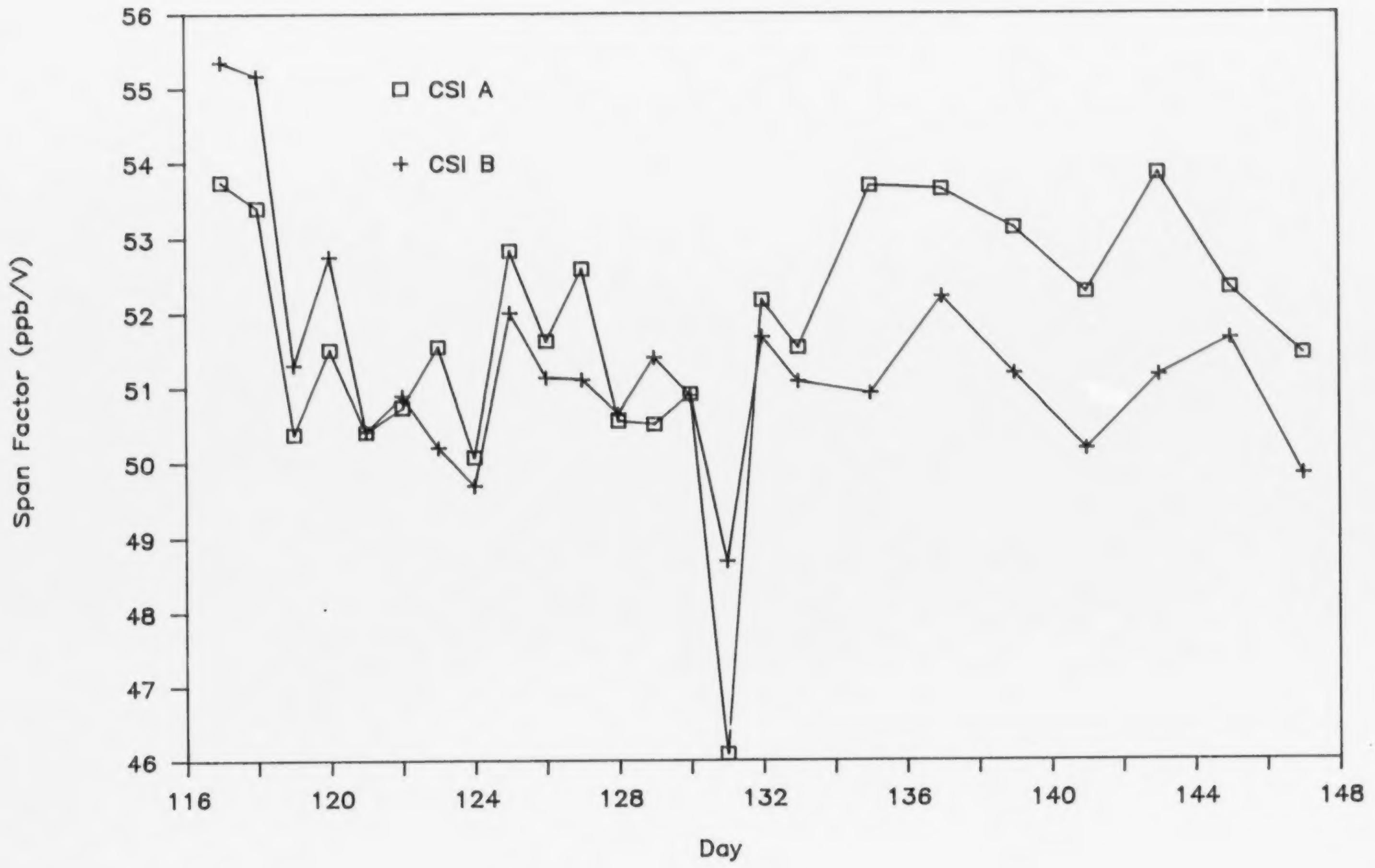

Figure 13. Span factors during the field evaluation for CSI 1600 NO_2 analyzers.

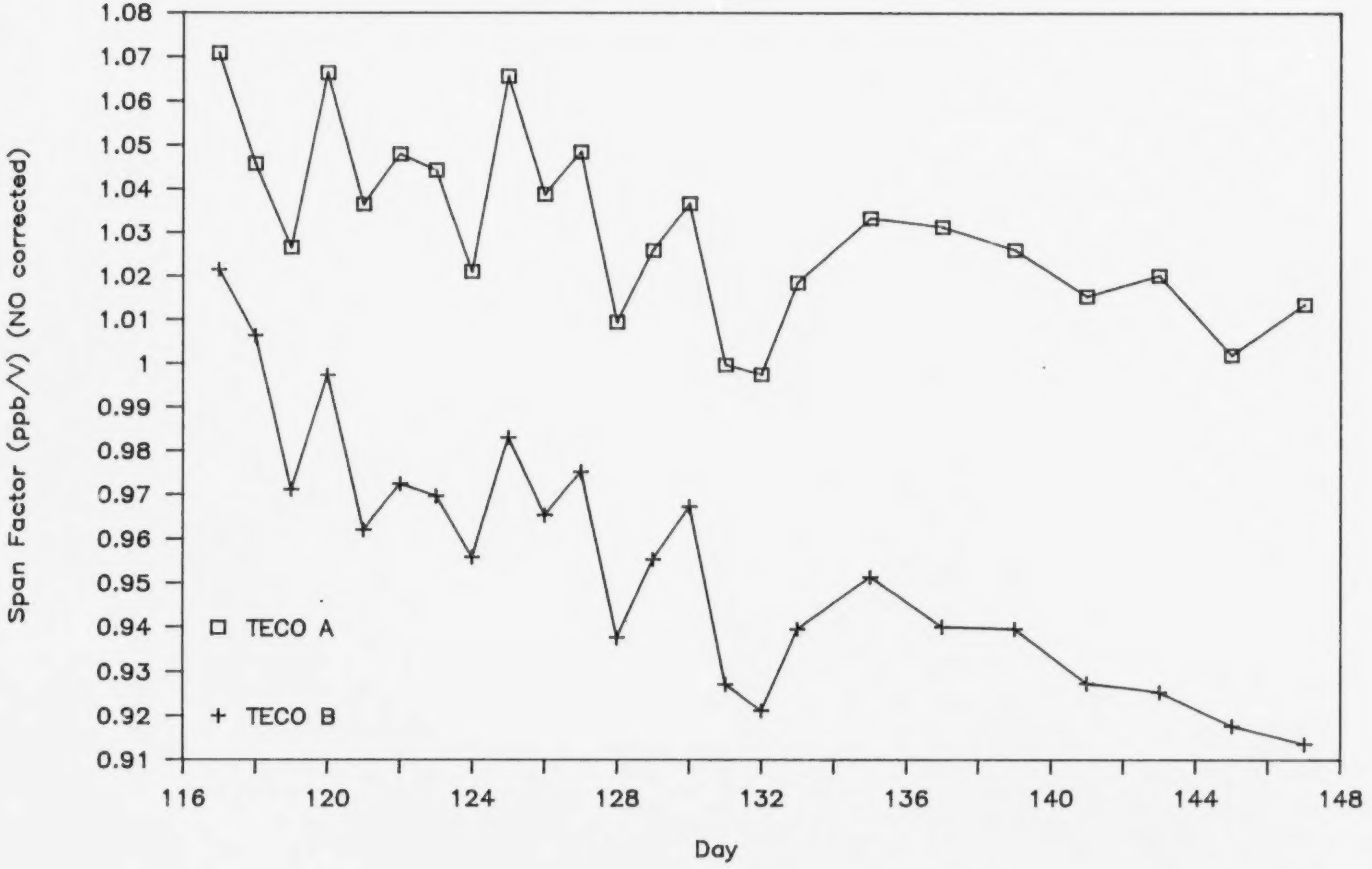

Figure 14. Span factors during the field evaluation for TECO 43S SO_2 analyzers.

A qualitative review of the span factors for the TECO 43S analyzers suggests a slight secular trend. Their span factors exhibit a general downward trend in time if the three days following the air conditioner failure are excluded. Simple linear regression (excluding these days) of the span factors against the Julian dates supports this observation. For TECO A, the regression has a slope of -1.39×10^{-3} ppb/volt-day with a r^2 of 0.49. Relative to the mean TECO A span factor of 1.035 ppb/volt, this slope corresponds to a span factor drift of -0.13%/day. For TECO B, the regression has a slope of -2.69×10^{-3} ppb/volt-day. Relative to the mean TECO B span factor of 0.960 ppb/volt, this slope corresponds to a span factor drift of -0.28%/day.

Multipoint Calibrations

In addition to the zero and span values discussed above, multipoint calibrations of both NO_2 and SO_2 analyzers were performed on April 26, May 10, and May 26 (Julian days 117, 131, and 147, respectively). Measurements were made at approximately 0% (zero air), 20%, 50%, and 80% of full-scale concentration. The calibration data are presented in Tables 37 and 38. The multi-point calibration data fall very nearly on a straight line for all analyzers. Simple linear regression yielded r^2 which ranged from 0.9966 to 1.000. As noted above, the station air conditioner failed on the afternoon of May 10 (day 131). This caused CSI A to fail during the measurement of the zero percent concentration. For this reason, the zero percent reading could not be used and the zero value was taken as the intercept of the regression line of the 20%, 50%, and 80% concentration points.

Response Times

As noted in the Laboratory Evaluation section, above, the LMA 3 analyzers have much better response times than the CSI 1600 analyzers. This was also noticed in the field measurements, where the LMA 3 analyzers' responses exhibited larger, short-term fluctuations than did the CSI 1600 analyzers. These short duration peaks were averaged out by the CSI 1600 analyzer. This phenomenon produced the interesting result that the actual field measurements (as opposed to calibration values) of the LMA 3 analyzers appear to be noisier than those of the CSI 1600 analyzers due to the superior response times of the LMA 3 analyzers, which more quickly tracks the local ambient fluctuations in the NO_2 concentration. In fact, LMA 3 has less noise than the CSI 1600 (see the Laboratory Evaluation section above). This could clearly be seen in the recorder output for the field calibrations, where the CSI 1600 analyzers exhibited higher noise than the LMA 3 analyzers.

Ambient Air Quality Measurements

The extrasensitive analyzers sampled ambient air during those portions of the field evaluation in which they were not being calibrated. Hourly mean concentrations were calculated from these measurements using the procedures described in Section 4. The purpose of these ambient air quality measurements was to produce matched sets of hourly mean NO_2 and SO_2 concentrations from which analyzers' precision estimates could be calculated. The CSI 1600 and LMA 3 analyzers produced 483 sets of matched hourly mean NO_2 concentrations during the period from April 26 through May

TABLE 37. MULTIPOINT CALIBRATION DATA

(a) Nitrogen Dioxide Analyzers

				Analyzer Response (V)			
Month	Day	Julian Date	$[NO_2]$ (ppb)	LMA A	LMA B	CSI A	CSI B
4	26	117	30.02	4.145	3.478	0.5876	0.5895
4	26	117	22.95	2.973	2.693	0.4400	0.4470
4	26	117	6.85	0.759	0.679	0.1380	0.1522
4	26	117	0.00	0.004	0.018	0.0158	0.0298
5	10	131	31.49	4.370	3.712	0.6652	0.6665
5	10	131	20.94	2.929	2.549	0.4361	0.4474
5	10	131	7.37	0.819	0.766	NA[a]	0.1509
5	10	131	0.00	0.012	0.036	NA[a]	0.0307
5	26	147	33.91	4.472	3.554	0.6671	0.7018
5	26	147	22.44	2.967	2.360	0.4421	0.4631
5	26	147	6.92	0.872	0.671	0.1361	0.1447
5	26	147	0.00	0.003	0.010	0.0093	0.0130

(b) Sulfur Dioxide Analyzers

				Apparent $[SO_2]$ (ppb)[b]		Response (V)	
Month	Day	Julian Date	True $[SO_2]$	TECO A	TECO B	TECO A	TECO B
4	26	117	9.242	9.612	9.530	9.185	9.435
4	26	117	4.800	4.883	4.864	4.673	4.764
4	26	117	2.052	2.087	2.079	2.102	2.079
4	36	117	0.000	0.000	0.000	0.209	0.107
5	10	131	7.931	8.215	8.152	8.389	8.888
5	10	131	4.560	4.681	4.654	4.783	5.072
5	10	131	2.062	2.120	2.107	2.126	2.268
5	10	131	0.000	0.000	0.000	0.173	0.097
5	26	147	8.247	8.510	8.451	8.456	9.236
5	26	147	4.758	4.863	4.839	4.737	5.137
5	26	147	2.049	2.090	2.081	2.065	2.196
5	26	147	0.000	0.000	0.000	0.061	-0.014

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[a] Point missing due to analyzer failure caused by air conditioning failure.
[b] SO_2 concentration corrected for NO interference.

(Continued)

TABLE 37. MULTIPOINT CALIBRATRION DATA (Continued)

(c) NO Channel for CSI 1600 Analyzers

				Analyzer Response (V)	
Month	Day	Julian Day	[NO] (ppb)	CSI A	CSI B
4	26	117	43.44	0.8245	0.8064
4	26	117	25.93	0.4883	0.4821
4	26	117	8.11	0.1417	0.1505
4	26	117	0.00	0.0105	0.0263
5	10	131	41.78	0.8539	0.8930
5	10	131	25.34	0.5102	0.5404
5	10	131	9.45	0.1685	0.1836
5	10	131	0.00	0.0035	0.0233
5	26	147	43.45	0.8712	0.8997
5	26	147	26.23	0.5156	0.5381
5	26	147	8.41	0.1662	0.1799
5	26	147	0.00	0.0116	0.0210

(d) NO_x Channel for CSI 1600 Analyzers

				Analyzer Response (V)	
Month	Day	Julian Day	[NO] (ppb)	CSI A	CSI B
4	26	117	43.44	0.8513	0.8531
4	26	117	25.93	0.5145	0.5260
4	26	117	8.11	0.1776	0.2033
4	26	117	0.00	0.0105	0.0504
5	10	131	41.78	0.8635	0.9155
5	10	131	25.34	0.5209	0.5665
5	10	131	9.45	NA (a)	0.2224
5	10	131	0.00	NA (a)	0.0542
5	26	147	43.45	0.8768	0.9204
5	26	147	26.23	0.5321	0.5595
5	26	147	8.41	0.1852	0.2035
5	26	147	0.00	0.0116	0.0427

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[a] Point missing due to analyzer malfunction due to air conditioner failure.

TABLE 38. MULTIPOINT CALIBRATION REGRESSIONS

Parameter	Analyzer	Julian Day	Slope (ppb/volt)	Intercept (ppb)	r^2
NO_2	CSI A	117	52.6417	-0.5941	0.9994
		131	46.0876	0.8347	1.0000 (a)
		147	51.3498	-0.2900	0.9999
	CSI B	117	53.8245	-1.4427	0.9996
		131	48.6922	-0.8212	0.9980
		147	49.0731	-0.4102	0.9998
	LMA A	117	7.2277	0.7131	0.9966
		131	7.0575	0.6046	0.9974
		147	7.5511	0.1208	0.9999
	LMA B	117	8.5002	0.3588	0.9985
		131	8.3786	0.1543	0.9979
		147	9.4880	0.1725	0.9997
SO_2	TECO A	117	1.0697	-0.1788	0.9999
		131	0.9939	-0.0903	0.9995
		147	1.0139	-0.0174	0.9997
	TECO B	117	1.0204	-0.0616	0.9998
		131	0.9243	-0.0440	0.9998
		147	0.9139	0.0602	0.9997
NO	CSI A	117	52.8783	0.0056	0.9993
		131	48.5851	0.4861	0.9989
		147	50.4554	-0.2130	0.9996
	CSI B	117	55.1598	-0.8341	0.9992
		131	47.3058	-0.2549	0.9982
		147	49.3560	-0.6973	0.9997
NO_x	CSI A	117	51.8970	-0.7884	0.9999
		131	47.9986	0.3441	1.0000 (b)
		147	50.3968	-0.7079	0.9999
	CSI B	117	54.2654	-2.7788	1.000
		131	48.0103	-1.9637	0.9990
		147	49.4607	-1.8208	0.9997

[a] Zero-percent value missing due to instrument malfunction. Regression is through 20-, 50-, and 80-percent values.

[b] Zero-and 20-percent values missing due to instrument malfunction. Regression is through the 50- and 80-percent values.

27, 1988. The TECO 43S and TECO 43A analyzers produced 463 sets of matched hourly mean SO_2 concentrations during the same period. Overall mean concentrations for the field evaluation are given in Table 39.

TABLE 39. OVERALL MEAN CONCENTRATIONS FOR AMBIENT AIR QUALITY MEASUREMENTS

Parameter	Analyzer	Overall Mean Concentration
NO_2	CSI A	13.022 ppb
	CSI B	13.314 ppb
	LMA A	11.309 ppb
	LMA B	10.512 ppb
SO_2	TECO A	1.691 ppb
	TECO B	1.653 ppb
	RTI-SO_2	1.398 ppb

It should be noted that the SO_2 data from the field evaluation were in good agreement with SO_2 data collected at the nearby EPA National Dry Deposition Network Site in Research Triangle Park. THe EPA site measured an overall mean SO_2 concentration of 1.61 ppb for the period from April 26 through May 24, 1988. (Rudolph D. Boksleitner, U. S. Environmental Protection Agency, personal communication, 1989.) The EPA site used filter packs to measure SO_2. The SO_2 value is based on extractable sulfate from both the nylon and Whatman post-filters.

A copy of the ambient air quality measurements from the field evaluation may be obtained by written request to the authors. Data from the trailer's ambient air quality analyzers and meteorological instruments are included for comparison purposes.

During periods of high NO_x concentrations, the hourly mean NO_x concentrations for the CSI 1600 analyzer listed in the data printout may not be as large as the sum of the CSI 1600 NO and NO_2 concentrations. This phenomenon is an artifact of the data processing program rather than a problem in the CSI 1600 analyzers. Some overranged, 2-minute NO_x voltges have been excluded from the calculation of the hourly average NO_x voltage, but the corresponding values for NO and NO_2 may be retained if they are not overranged. This situation is possible because the NO signal is subtracted from the NO_x signal before amplification where overranging occurs. Only the hourly average NO_x concentrations are in error during these periods.

In addition to the measured data, calculated data are listed in the printout. Corrected data for the TECO 43S analyzers are calculated by subtracting the NO interference concentration from the uncorrected SO_2

concentrations. Concentration differences are calculated for the extrasensitive analyzers according to the following formulas:

$$LD\text{-}NO_2 = LA\text{-}NO_2 - LB\text{-}NO_2$$
$$CD\text{-}NO_2 = CA\text{-}NO_2 - CB\text{-}NO_2$$
$$TD\text{-}SO_2 = COR43SA - CORR43SB$$

Concentration Differences and Precision Estimates

The intra-model precision of the extrasensitive analyzers can be estimated from the ambient air quality measurements because two analyzers from each analyzer model were included in the field evaluation. The precision is calculated by dividing the standard deviation of the concentration difference between the two analyzers by the square root of two. Table 40 presents daily and overall means and standard deviations of the concentration differences. The overall means and standard deviations are calculated from the hourly concentration differences and not from the daily mean differences. As a result, the precision estimates are for the entire field evaluation. The daily precision estimates are smaller than the overall precision in those cases in which the concentration differences vary significantly from day-to-day.

It should be noted that these precision estimates are somewhat in error because of the implicit assumption that the precision is independent of concentration. The results of the laboratory evaluation show that the precisions of the LMA 3 and TECO 43S analyzers are concentration dependent.

A qualitative review of the concentration differences in the printout suggests that their magnitude is proportional roughly to the concentrations. Because the concentrations varied considerably during the field evaluation, the standard deviations of the concentrations are larger than they would be under a constant NO_2 concentration. This observation suggests that these precision estimates should take the concentration dependence into account.

It should also be noted that the precision estimates for the LMA 3 analyzers may be influenced by the short-term variability of the atmospheric NO_2 concentration. The trailer's data acquisition system collects instantaneous voltage readings at 2-minute intervals. The response time of the LMA 3 analyzers is less than or equal to this interval. If the atmospheric NO_2 has considerable variability during this interval and if the responses of the two analyzers are not perfectly synchronized, the standard deviation of the instantaneous concentration difference would be larger than it would be under a constant NO_2 concentration. The magnitude of this effect is greatly reduced for the difference between hourly average concentrations.

The overall mean concentration difference for the LMA 3 analyzers is 0.733 ppb. On a daily basis, the mean concentration difference varies from -1.577 to 1.793 ppb. The pattern of the day-to-day variation in the mean concentration differences parallels the pattern of the day-to-day variation in LMA B's span factor. The two phenomena appear to be related in some manner.

TABLE 40. DAILY AND OVERALL MEANS AND STANDARD DEVIATIONS OF THE CONCENTRATION DIFFERENCES BETWEEN PAIRED EXTRASENSITIVE ANALZYERS

			LMA 3 NO_2		CSI 1600 NO_2		TECO 43S SO_2	
Month	Day	Julian Day	Mean Diff. (ppb)	Std. Dev. (ppb)	Mean Diff. (ppb)	Std. Dev. (ppb)	Mean Diff. (ppb)	Std. Dev. (ppb)
4	26	117	0.286	0.130	0.193	0.407	0.056	0.018
	27	118	0.593	0.091	-0.088	1.039	0.043	0.024
	28	119	0.640	0.149	-0.372	0.564	0.059	0.023
	29	120	0.425	0.913	-0.587	0.598	0.060	0.036
	30	121	1.123	0.421	-0.411	0.504	-0.004	0.028
5	1	122	1.165	0.537	-0.357	0.362	0.068	0.031
	2	123	0.450	1.017	-0.590	0.514	0.066	0.025
	3	124	0.608	0.317	-0.350	0.187	0.037	0.018
	4	125	0.300	0.795	-0.455	0.286	0.018	0.016
	5	126	1.354	0.488	-0.434	0.261	0.061	0.061
	6	127	2.006	0.265	-0.453	0.383	0.042	0.025
	7	128	1.438	0.575	-0.622	0.731	0.027	0.021
	8	129	1.793	0.843	-0.792	0.474	-0.008	0.012
	9	130	-1.577[a]	1.901[c]	-0.415	0.260	-0.002	0.015
	10	131	--[b]	--	--	--	--	--
	11	132	-0.541	1.457	-0.584	0.667	0.035	0.057
	12	133	0.466	0.400	-1.134	0.619	0.112	0.020
	13	134	0.739	0.485	-0.688	0.535	0.072	0.047
	14	135	0.181	0.216	-0.072	0.293	0.036	0.016
	15	136	0.420	0.374	-0.128	0.305	0.011	0.015

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[a] The pump tubing was changed in the LMA 3 analyers on this date.
[b] Data for Day 131 was discarded because of the failure of the trailer's air conditioner.
[c] Questionable value because the pump tubing was changed on this date.

(Continued)

TABLE 40. DAILY AND OVERALL MEANS AND STANDARD DEVIATIONS OF THE CONCENTRATION DIFFERENCES BETWEEN PAIRED EXTRASENSITIVE ANALZYERS (Cont'd)

			LMA 3 NO_2		CSI 1600 NO_2		TECO 43S SO_2	
Month	Day	Julian Day	Mean Diff. (ppb)	Std. Dev. (ppb)	Mean Diff. (ppb)	Std. Dev. (ppb)	Mean Diff. (ppb)	Std. Dev. (ppb)
5	16	137	0.769	0.219	-0.088	0.186	0.005	0.027
	17	138	0.742	0.447	-0.069	0.236	0.008	0.024
	18	139	1.256	0.455	0.176	0.346	0.044	0.019
	19	140	1.716	0.574	0.092	0.427	0.061	0.060
	20	141	1.349	0.561	0.147	0.541	0.016	0.016
	21	142	1.389	0.967	0.035	0.314	0.024	0.031
	22	143	1.035	0.449	0.131	0.229	0.045	0.021
	23	144	-0.321[a]	1.177[b]	0.212	0.149	0.002	0.045
	24	145	-0.035	0.789	-0.255	0.335	0.010	0.028
	25	146	0.279	0.111	0.042	0.327	0.007	0.021
	26	147	0.343	0.125	0.187	0.260	0.027	0.026
Overall Values[c]			0.733	0.930	-0.259	0.554	0.036	0.042
Precision[d]				0.658		0.392		0.030

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[a] The pump tubing was changed in the LMA 3 analyzers on this date.

[b] Questionable value because the pump tubing was changed on this date.

[c] The overall values are calculated from the hourly concentration differences, and not from the daily mean concentrtion differences.

[d] Precision = overall standard deviation/square root of 2.

The overall mean concentration difference over the entire field evaluation for the CSI 1600 analyzers is -0.259 ppb. On a daily basis, the mean concentration difference varies from -1.134 to 0.212 ppb. There appears to be a shift in the daily mean concentration differences that is associated with the time of the air conditioner failure. The mean of these daily mean values is -0.410 ppb before the failure and is -0.125 ppb after the failure. The daily mean values exhibit less variability before the failure (s = 0.238 ppb) than after the failure (s = 0.357 ppb).

The overall mean concentration difference for the TECO 43S analyzers is 0.036 ppb. On a daily basis, the mean concentration difference varies from -0.008 to 0.112 ppb. Relatively little day-to-day variation is seen in these values.

The overall standard deviation of the concentration difference for the LMA 3 analyzers is 0.930 ppb which results in a precision estimate of 0.658 ppb. The standard deviation varies from 0.091 to 1.901 ppb on a daily basis. The values for Days 130 and 144 are questionable because the pump tubing was changed and LMA B's span factor shifted radically on these days.

The overall standard deviation of the concentration difference for the CSI 1600 analyzers is 0.554 ppb which results in a precision estimate of 0.392 ppb. The standard deviation varies from 0.149 to 1.039 ppb on a daily basis.

The overall standard deviation of the concentration difference for the TECO 43S analyzers is 0.042 ppb which results in a precision estimate of 0.030 ppb. The standard deviation varies from 0.012 to 0.061 ppb on a daily basis.

Principal Component Analysis

Estimates of the effective operating precision of the extrasensitive analyzers were obtained from the field evaluation data using principal component analysis. The nitrogen dioxide data were run on EPA's program and the sulfur dioxide data were run on RTI's program. Because the programs require data from a minimum of three analyzers to operate, analysis of the sulfur dioxide data included data from the trailer's TECO 43A analyzer. Too little data were obtained from the trailer's NO_x analyzer for them to be included in the analysis of the nitrogen dioxide data. Because the programs cannot handle missing values, all data from a given hour were omitted if any analyzer's hourly average concentration was missing.

The basic model for principal component analysis is:

$$[C_i] = A_i + B_i[C_t] + E_i$$

where C_i = the measured concentration for the i-th analyzer,
A_i = the constant bias of the i-th analyzer,
B_i = the proportional bias of the i-th analyzer,
C_t = the true concentration, and
E_i = the effective operating precision of the i-th analyzer.

E_i^2, the effective variance of the i-th (or the effective operating precision) analyzer is the sum of the intra-model precision and the variance associated with an assumed random interference effect. Principal component analysis cannot estimate A_i or B_i. However, it can estimate the ratio of the B_i for any two analyzers by the ratios of the i-th eigenvectors associated with the largest eigenvector of the sample covariance matrix for the data. It is primarily designed to yield estimates of the E_i. Lower and upper 95-percent confidence limits for E_i and an estimated minimum detection limit are also calculated by the EPA program, but not by the RTI program.

Principal component analysis has a number of assumptions which must be satisfied if its results are to be statistically valid. Among these assumptions are:

- At least three analyzers' data must be compared;
- The range of the C_i must be very, very large relative to the value of E_i;
- The value of E_i must be constant for all C_t (and not proportional to C_t);
- The interference effect is truely random (and not proportional to C_t); and
- The methods to be compared must be sufficiently different in their sensitivity to the various interfering substances.

These assumptions are violated to some degree by the extrasensitive analyzer data from the field evaluation. Accordingly, the results of the principal component analysis of this data are somewhat questionable. Nevertheless, the results are presented because they may yield some useful information concerning the extrasensitive analyzers.

A summary of the principal component analysis for the extrasensitive analyzer data from the field evaluation is given in Table 41. The results for the NO_2 analyzers will be considered separately from those for the SO_2 analyzers.

A total of 483 sets of NO_2 data were run through the program. The difference in the mean concentration for the LMA 3 analyzers is 0.797 ppb which compares well with the mean concentration difference of 0.733 ppb given in Table 39. The corresponding value for the CSI 1600 analyzers is -0.292 ppb which compares well with the value of -0.259 ppb given in Table 39. The effective operating precisions for the two LMA 3 analyzers are 0.504 and 0.626 ppb, which compare relatively well with the intra-model precision of 0.658 ppb given in Table 40. These precision estimates may be partially compromised by the span factor drift that was observed in LMA B. The frequent calibration of these analzyers tended to reduce the effect of this drift on the NO_2 concentration measurements and the precision estimates obtained from these analyzers. The corresponding values for the CSI 1600 analyzers are 0.284 and 0.185 ppb, which are appreciably lower than the intra-model precision of 0.392 ppb given in Table 40.

Comparison of the results given in Table 41 with those given in Table 40 suggests that principal component analysis is relatively accurate in estimating the precision of the extrasensitive analyzers. The results for the CSI 1600 analyzers from the principal component analysis may be lower than the true precision for these analyzers because two similar analyzers with similar interference effects are being compared. Principal component analysis has the implicit assumption that the analyzers must be sufficiently different in their sensitivity to various interfering substances.

TABLE 41. SUMMARY OF PRINCIPLE COMPONENT ANALYSIS FOR THE EXTRASENSITIVE ANALYZER DATA FROM THE FIELD EVALUATION

(a) Nitrogen Dioxide Analyzers

	LMA A	LMA B	CSI A	CSI B
Mean Concentration (ppb)	11.309	10.512	13.022	13.314
Eigenvector Elements for Largest Eigenvalue	0.4947	0.4897	0.4968	0.5182
Operating Precision (ppb)	0.504	0.626	0.284	0.185
Upper Limit (ppb)	0.596	0.733	0.350	0.245
Lower Limit (ppb)	0.432	0.541	0.235	0.144
Estimated Detection Limit (ppb)	0.973	1.079	0.746	0.624

(b) Sulfur Dioxide Analyzers

	TECO A[a]	TECO B[a]	RTI-SO_2
Mean Concentration (ppb)	1.691	1.653	1.398
Eigenvector Elements for Largest Eigenvalue	0.5902	0.5748	0.5667
Operating Precision (ppb)	0.0003	0.0003	0.111
Upper Limit (ppb)	- - -[b]	- - -	- - -
Lower Limit (ppb)	- - -[b]	- - -	- - -
Estimated Detection Limit (ppb)	- - -[b]	- - -	- - -

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[a] Values corrected for interference from nitric oxide.

[b] These calculations were not performed by RTI's program.

It should be noted that the effective operating precisions for the CSI 1600 analyzers given in Table 41 are approximately an order of magnitude lower than the value of 2.7 ppb that was obtained by Holland and McElroy for the same model NO_2 analyzer (25). It is unclear why the two precision estimates are so different, but the explanation may be associated with the ranges on which the analyzers were operated. Holland and McElroy analyzed a data set that was obtained on the analyzers' 0-500 ppb range, and this study analyzed a data set that was obtained on the analyzers' 0-50 ppb range. Differences in other operating parameters (perhaps associated with the data acquisition systems or the data processing programs) may also explain the differences in the precision estimates.

Difficulties were encountered in running the SO_2 data on EPA's program. For the sake of expediency, these data were run on an alternate principal component analysis program that RTI had on hand. The RTI program had been tested using the NO_2 data and produces results that are nearly identical with those of the EPA program. However, the RTI program is not as extensive as the EPA program, and upper and lower limits and estimated detection limits were not calculated.

A total of 463 sets of SO_2 data were run on the RTI program. The corrected data for TECO A and TECO B were compared to the data for RTI's TECO 43A analyzer. The difference in the mean concentrations for the TECO 43S analyzers is 0.039 ppb, which compares well with the mean concentration difference of 0.036 ppb given in Table 40. The effective operating precisions of the two TECO 43S analyzers are 0.0003 and 0.0003 ppb, which are approximately two orders of magnitude less than the intra-model precision of 0.030 ppb given in Table 40. The corresponding value for RTI's TECO 43A analyzers is 0.111 ppb. This value is probably more accurate, although no other precision estimate for the TECO 43A analyzer is available for comparison.

The very low values of the effective operating precision for the TECO 43S analyzers are likely to be an artifact of principal component analysis. If the data for these two analyzers are very closely matched and if the data for the TECO 43A analyzer is not as well matched, principal component analysis would then tend to place more weight on the data for the two extrasensitive analyzers. Very low precision estimates for the extrasensitive analyzers would be the result. This outcome is a result of the violation of the implicit assumption that the methods being compared must be sufficiently different in their sensitivity to various interfering substances. It should be noted that this outcome is similar to a negative precision estimate that Fung and Hunter obtained in their principal component analysis of a constructed data set (27).

REFERENCES

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